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FINAL REPORT

on

TRACE MATERIAL GENERATION RATE SIMULATOR.
TASK B: STUDY OF GENERATION RATE PATTERNS

to

HONEYWELL, INC.
AERONAUTICAL DIVISION

from

NORTH STAR RESEARCH AND DEVELOPMENT INSTITUTE
May 28, 1965

INTRODUCTION AND SUMMARY

This document presents the methods and results of studies on trace-material generation rate patterns anticipated in the habitable area of a spacecraft on a 14-day mission. The chief objective of the research was to provide programs for operation of a trace material control unit (TMCU) which would simulate both actual generation rates and equivalent rates modified to account for the presence of trace material sinks. A second objective was to disclose any inadequacies in the inventory of a space capsule, in the identification and characterization of trace materials, and in the kinetics of gas evolution which should be remedied to permit a more reliable study of generation rate patterns.

Research methodology and the results obtained by application of the methodology to the problem of estimating generation rate patterns for trace

materials are presented. The trace-material sources are the material, equipment, and the men in a six-cubic-meter capsule designed for a 14-day lunar mission.

The first part of the report is an exposition of the rate-controlling mechanism for the gassing of organic materials. A diffusion-controlled mechanism provides the mathematical model for calculation of gassing rates versus time. It is applied to the components of the stabilization and control system (SCS) to arrive at trace-material generation rates. Correlation of the findings with data on analyzed atmospheres after Mercury flights led to an estimate of the total amount of electronic gear, and to estimates of the kind and rate of generation of other trace materials not associated with electronic gear. Volatile materials of biological origin were added to the listing. Results of all calculations are provided in tabular form in the report.

A scheme was devised to use available numerical data on the toxicity of materials to obtain "relative toxicity" ratings. Some trace materials could then be substituted for others to arrive at a smaller list of materials for use in the TMCU. The "relative toxicity" ratings have been tabulated.

The last part of the report presents a methodology for simulating the action of trace-material sinks in order to develop programs for the TMCU. Programs designed to simulate closed systems with and without trace-material sinks require the actual use of open loops. The programs are, in general, within the design capabilities of the trace-material control unit.

RECOMMENDATIONS FOR ADDITIONAL WORK

The current analysis was undertaken with the object of arriving at trace material generation rates based on available information. It was, and still is, apparent that data are lacking for complete and accurate development of generation rates, and for the making of meaningful toxicity predictions.

To gather the requisite data on generation rates, three major alternatives may be considered. These are:

1. Analysis of the accumulation of gaseous contaminants in a space capsule carried through a simulation of actual use.
2. Development of understanding based on mathematical and experimental analyses of the actual processes contributing to gaseous contamination occurring in each component material.
3. Development of empirical data on gaseous output from each component material.

The first alternative is surely the easiest, but at the same time the least satisfactory. It does not provide the basic data which will permit prediction of effects on gaseous contamination when alterations are made in materials, components, or operating conditions.

The second alternative is ideal but may or may not be practical. A first step would be to examine its practicality. We visualize that its pursuit could progress through the following phases:

1. Mathematical treatment of one or two cases in which assumptions are made as to the existence of several concurrent processes (oxidation, thermal degradation, and diffusion). Such an analysis would serve to examine the ease with which a detailed understanding of the processes involved could be put to use, if available. It would also serve to identify the important variables to which attention should be given in gathering and using experimental data.
2. A complete inventory of all materials, equipment, and processes in Apollo C/M.
3. Forecasts of the expected temperature profile as a function of time for each material in the inventory. This is necessary as a guide to testing procedures and as part of the information needed to predict gassing rates.
4. Information on weight, surface area, and volume of each item of the inventory together with information on proximity to diffusion barriers which will restrict access of outgassed material to the atmosphere.
5. Measurements of outgassing designed to give information on the processes involved and their rates. This would mean that data should be gathered at a series of temperatures under conditions such that diffusion rates are not a limiting factor. This could be accomplished by making measurements of outgassing of very thin sheets or of powders. Measurements should be made in the presence and in the absence of oxygen to distinguish between thermal degradation and oxidative processes. By repeating studies using thicker pieces of known volume, diffusion rates could be calculated.

Such an approach would give basic data which would be interpolated and extrapolated with confidence as alterations in components are made (providing the same materials are used). If the labor of such an approach

appears overwhelming after completion of step one, or even before its completion, then the third alternative approach should be undertaken.

This approach would require:

1. A complete inventory of all materials, equipment, and processes in Apollo C/M.
2. Forecasts of the expected temperature profile as a function of time for each material in the inventory. This is necessary as a guide to testing procedures and as part of the information needed to predict gassing rates.
3. Studies of outgassing of actual components of suitable samples of actual components. Such studies would probably provide sufficient data for predictive purposes if it included measurements of gases produced at three different time intervals at each of three temperatures. In actuality, it probably would not be necessary to carry out studies on each component. Initial probes would undoubtedly show the gas contribution from some classes of materials to be negligible.

This third alternative would not be capable of as great extrapolation as the second. From the practical standpoint, it may be more attractive, and could be undertaken instead of the second alternative.

Contaminants arising from biological sources similarly require additional attention before their identity and quantity can be predicted with confidence. The following units of work are recommended:

1. A literature search in depth for additional information on the identity and generation rates of volatile materials from biological sources. The estimates of these materials set forth in this report have been based largely on secondary sources. A study in which original sources could be studied and compared in detail would yield more meaningful estimates. Interviews with investigators who are actively concerned themselves with such

questions as the identity of the components of sweat, the effect of bacterial action on sweat, and the identity of flatus components would be particularly helpful in sharpening and evaluating the estimates.

2. An experimental study of expired air to identify and measure normal trace contaminants. Because of the large volume of respiratory air, the presence of very small amounts of foreign chemical species could make a large contribution to the contamination of the space-capsule atmosphere. Very little evidence of systematic investigation of this source was evident from our exploration of the literature. Such studies would seem to merit high priority. Some ideas on the necessary refinement of experimental approaches have been conceived.
3. A study to identify and measure the unidentified components of flatus. Dr. Murphy of the United States Department of Agriculture had estimated that as much as one percent of flatus components remain unidentified. This could be an important source of contamination and is deserving of continued research emphasis.
4. A study of apocrine sweat. In work on sweat constituents little attention has been given to apocrine sweat. Systematic studies of its constitution are needed.

These comments relate to the identification and quantification of those materials which might predictably appear as contaminants of the space capsule atmosphere. The assessment of their significance in terms of effects on man represents an area where very little meaningful work is available. This is especially true when one considers possible additive and synergistic effects and when one considers possible effects on behavior and efficiency. Studies in which the effects of combinations of the significant contaminants on behavior as well as upon the usual indicators of toxicity are called for. The initial experiments should be in animals with final confirmation of safety in man.

RESULTS

Gassing of Organic Materials

When the partial pressure of trace materials in the atmosphere is low, the rate-controlling factor in the degassing rate is the mechanism by which these volatiles are released. This mechanism is not unique. For saturated systems, there is a constant "drying" rate corresponding to evaporation as from a liquid of constant area. This is followed by a falling rate over a period of time during which the evaporation rate is proportional to the fraction of the surface which is wet. Finally, there is another period of falling rate during which liquid evaporates from the surface as fast as it can get there by diffusion from the interior of the solid.

Materials acceptable for space-travel missions will gas according to some modification of the last mechanism. This follows because baking of coatings and "running in" of equipment prevents the attainment of saturation of the surface with volatile materials. The modification of simple diffusion arises from slow, but continuous, generation of the same or new contaminants by thermal degradation and oxidation. These fresh trace materials must also be lost by a diffusion process, except for a small fractional part generated at the surface. Thus, the over-all rate of generation of trace materials will be diffusion-controlled.

Diffusion-controlled gassing will react to temperature changes by the obvious change in magnitude of the diffusion constant and by changes in

rate of production of trace materials by oxidation and thermal degradation. For a given temperature the trace contaminants will be lost according to a particular solution of Fick's law of diffusion for nonstationary state of flow. The solution used for this program⁽¹⁾ is adapted to the empirical gassing data available and to the geometry of the test materials. The concept used is that of drying a slab of material from two sides. It is, of course, only an approximation in view of the variable geometry of test samples and of materials used in a spacecraft. However, it will define the general exponential decline with time of trace contaminant content of a material:

$$\log \left(\frac{Q_t}{Q_0} \right) \approx \log \left(\frac{8}{\pi^2} \right) - \frac{\pi^2 D t}{9.2 a^2} \quad [1]$$

where Q_t = average concentration remaining at time t

Q_0 = initial uniform concentration

a = thickness

D = diffusion constant

t = time

Use of the above equation serves two purposes. First, the gassing process can be studied as a diffusion-controlled process for materials on which gassing data are available. Second, gassing rates can be estimated for specific time intervals and for different temperatures. The accuracy of

estimation will be unknown in the case of samples of varying geometry undergoing a wide variety of decomposition reactions. A more accurate procedure could be followed in a kinetic study of one material.

The first objective -- showing that all materials gas according to a diffusion-controlled mechanism -- was met by showing: (1) that only random deviations exist in the relative rates of outgassing, and (2) that all the relative rates of outgassing conform to the pattern of equation [1]. The term "relative rate" here permits use of data based on samples of different materials with different Q_0 values and different geometries. The second objective -- estimating gassing rates for different temperatures over the time interval of the Apollo mission -- was met by using a reasonable energy of activation for diffusion, 6000 cal per mole, and by assuming no change in geometry between test samples and materials in the spacecraft. It is apparent that experimental kinetic studies are required to determine the temperature coefficients of specific reactions of thermal degradation and oxidation, and their contributions to changes in gassing rates with temperature.

Rate Controlling Mechanism for Gassing

Oven weight-loss data versus time were used to examine the random variation of relative rates of weight loss among all the materials studied in Honeywell's program⁽²⁾ of gassing testing for Apollo C/M Stabilization and Control System. The measurable weight losses for seven days at 350°F ranged from 0.1 to 68 percent by weight. The relative rate of weight loss between one and seven days was defined as the difference between the logarithms of percentage weight loss at these two times. Plotted against percentage weight loss after seven days in Figure 1, the relative rates show a random pattern. This suggests that the variations are due to experimental error rather than to a given mechanism. There is no evidence for more than one rate-controlling process, and the data can be represented as well by a single process, say diffusion, as by several.

To demonstrate this point further, the same relative rates were plotted on probability-log scales in Figure 2. The cumulative percentage of samples refers to those samples reported in the earlier testing program⁽²⁾. Note that the random nature of data in Figure 1 is confirmed by the organized pattern in Figure 2. Moreover, the relative gassing rates for different samples of one generic material (an epoxy designated as 6020) are scattered over the entire line in Figure 2. Since it is reasonable to assign only

one rate-controlling mechanism to one generic material, and since the scatter of data is no greater for the several materials than for the one material, it therefore, seems appropriate to assign only one rate-controlling mechanism to gassing of all the materials tested.

Probably the most obvious rate-controlling mechanism to consider is diffusion. Accordingly, the data on oven gassing were normalized by treatment according to equation [1]. This was aided by a redefinition of terms:

Q_0 = extrapolated value for weight loss in percent at
infinite time,

Q_t = weight loss in percent at time, t .

The following treatment was applied then to the oven test data for the more limited number of organic materials in the Stabilization and Control System.

By a series of approximations, a Q_0 value was selected for each material such that plots of $\log (Q_t/Q_0)$ versus time intercepted the log axis near $8/\pi^2$ as defined by equation [1]. All data conformed reasonably well to this treatment. The results supplied a bonus by indicating which materials were undergoing almost total degradation; for example, one material had a Q_0 value of 91 percent.

The chief use made of equation [1] was to calculate weight loss for any time interval. This was critical to the program because time zero for a space mission is not time zero for manufacture of a plastic or coating of

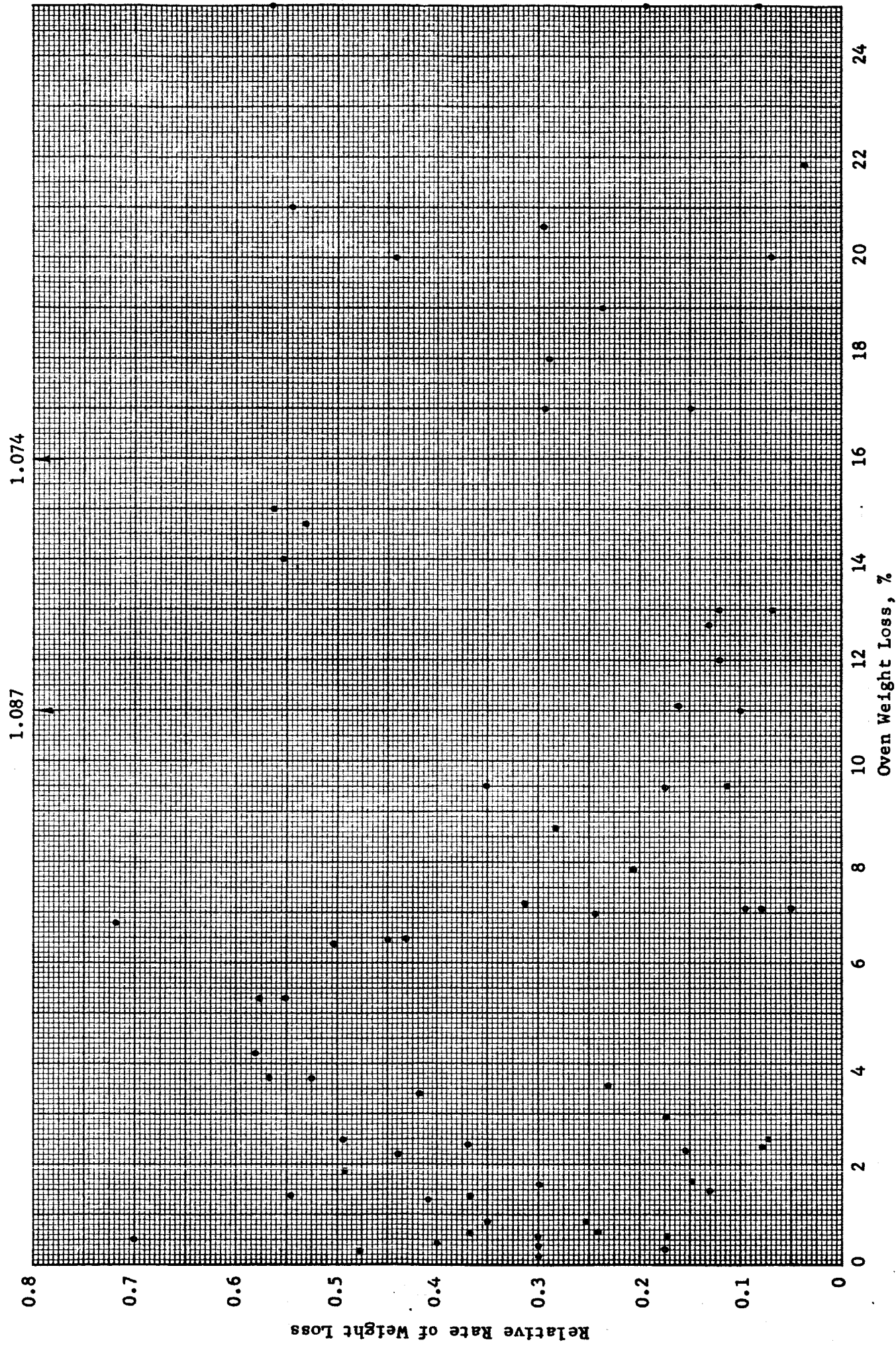


FIGURE 1 RELATIVE RATE OF WEIGHT LOSS AND ACTUAL WEIGHT LOSS IN OVEN TEST FOR VARIOUS MATERIALS IN SCS

Materials are identified by name in Table 1.
Material identification number indicates
relative rate for that material.

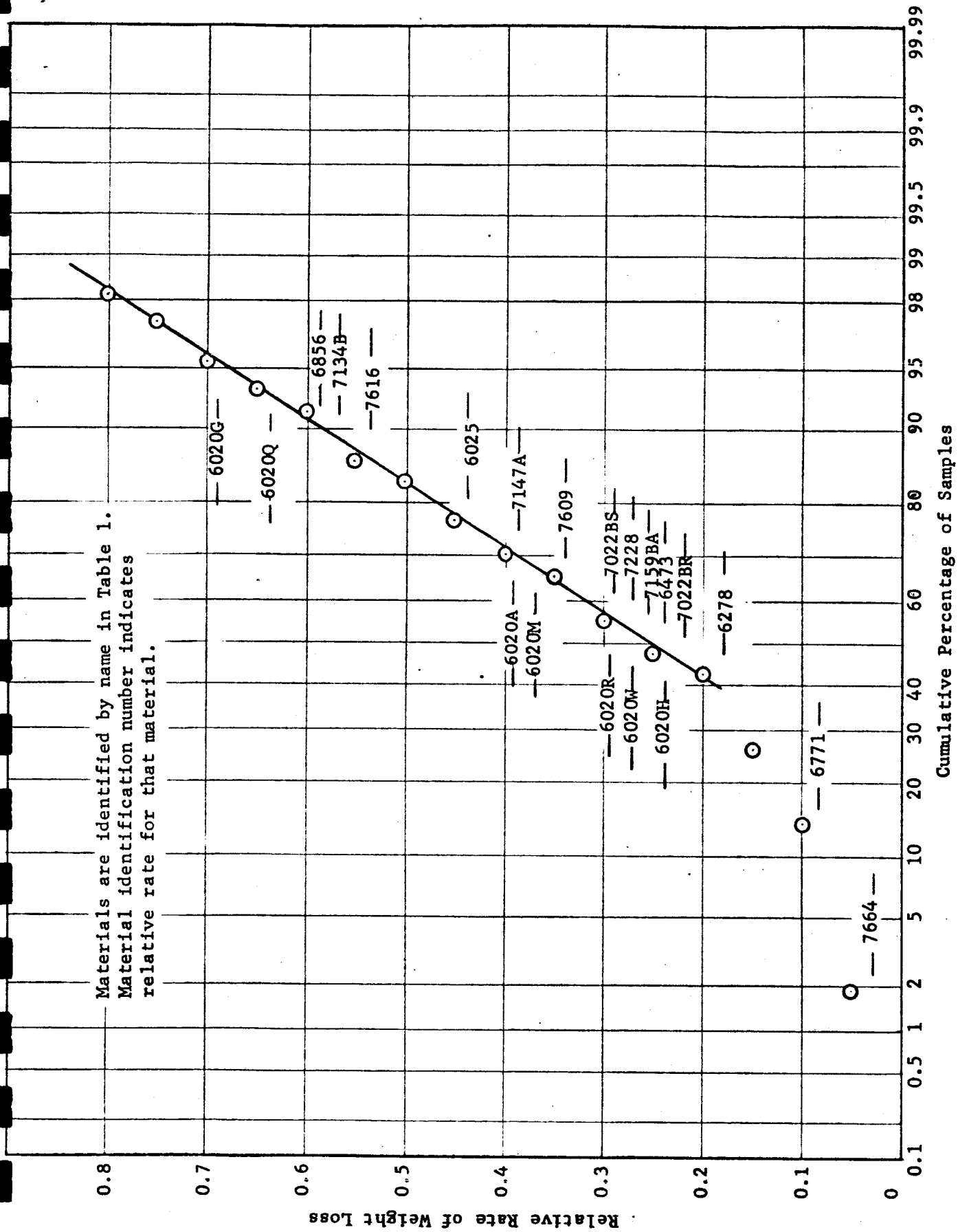


FIGURE 2 DISTRIBUTION OF OVEN WEIGHT LOSS DATA FOR VARIOUS MATERIALS IN SCS

an electrical component. Rather, it is the beginning of a 14-day period following approximately 1000 hours of operation of each system during mortality, running-in, and check-out tests. The period selected for this study was the period between 40 and 54 days after manufacture.

Table 1 contains the gassing rates calculated from oven weight-loss tests at 350°F. These rates are reported in day^{-1} , i.e. the slope of equation [1]. The table also includes calculated rates for 150°F based on an energy of activation of 6000 cal per mole. This temperature coefficient is significant providing there is no change in the geometry of the materials; with no geometry change, the diffusion constant is the only temperature-sensitive term in the slope of equation [1]. One recognizes but does not account for the higher temperature coefficient which is characteristic of the inherent processes of oxidation and thermal degradation.

It is difficult to estimate the reliability of the temperature correction. The selected energy of activation is reasonable for a diffusion process, however, and there were no experimental data at low temperature from which an energy of activation could be calculated. There are, in fact, gassing data for near 200°F based upon single points in time -- two days usually. The relationship between weight loss during seven days at 350°F and two days at 200°F is so tenuous (Figure 3), that calculations based on oven test data at 350°F and the assumed ΔE are preferred over use of the gassing data at 200°F.

TABLE 1

GASSING RATES FOR MATERIALS IN SCS BASED ON
OVEN WEIGHT LOSS DATA*

Material Name	Spec. No.	Q ₀ , Percent	Intercept	$n = \frac{\pi^2 D t}{9.2 a^2}, \text{ Day}^{-1}$		Total Gassing Rates at 150°F Between 40 and 54 Days (Percent)
				350°F	150°F	
Glass epoxy laminate	6473	1.8	0.80	1.75×10^{-2}	0.2×10^{-2}	0.075
Glass epoxy varnish	7134B	24	0.90	2.445×10^{-2}	0.275×10^{-2}	1.42
Fiberglass tape	6771	1.55	0.78	2.29×10^{-2}	0.25×10^{-2}	0.074
Lubricant	6762	Estimated from gassing test data				45.8
Silicone rubber	7147A	3.1	0.81	7.9×10^{-2}	0.88×10^{-2}	0.276
Polyester enamel	7664	90.77	0.81	0.346×10^{-2}	0.039×10^{-2}	0.80
Epoxy glass laminate	7560	Estimated from gassing test data				0.04
Nylon tying cord	7022	49	0.81	1.31×10^{-2}	0.15×10^{-2}	1.63
Polyester tape	6856	7.5	0.95	7.34×10^{-2}	0.825×10^{-2}	0.778
Epoxy adhesive	6020G	0.75	0.93	6.25×10^{-2}	0.7×10^{-2}	0.074
Silicone adhesive	7228	3.5	0.81	2.55×10^{-2}	0.29×10^{-2}	0.144
Urethane foam	7616	7.0	0.935	4.23×10^{-2}	0.426×10^{-2}	0.567
Acrylic	6025	4.4	0.84	8.18×10^{-2}	0.92×10^{-2}	0.407
Rubber adhesive	6733	Estimated from gassing test data				0.6
Epoxy foam	7609	0.85	0.85	2.65×10^{-2}	0.3×10^{-2}	0.048
Photographic film	7570	Estimated from gassing test data				0.43
Marking ink	7765	Neglect because of low weight				
Acrylic enamel	7541	Neglect because of low weight				
Viton A	7159	0.42	0.805	2.72×10^{-2}	0.306×10^{-2}	0.024

*Note that where oven test data were erratic or not available, estimates were based on measured weight loss in gassing-test data for 200°F.

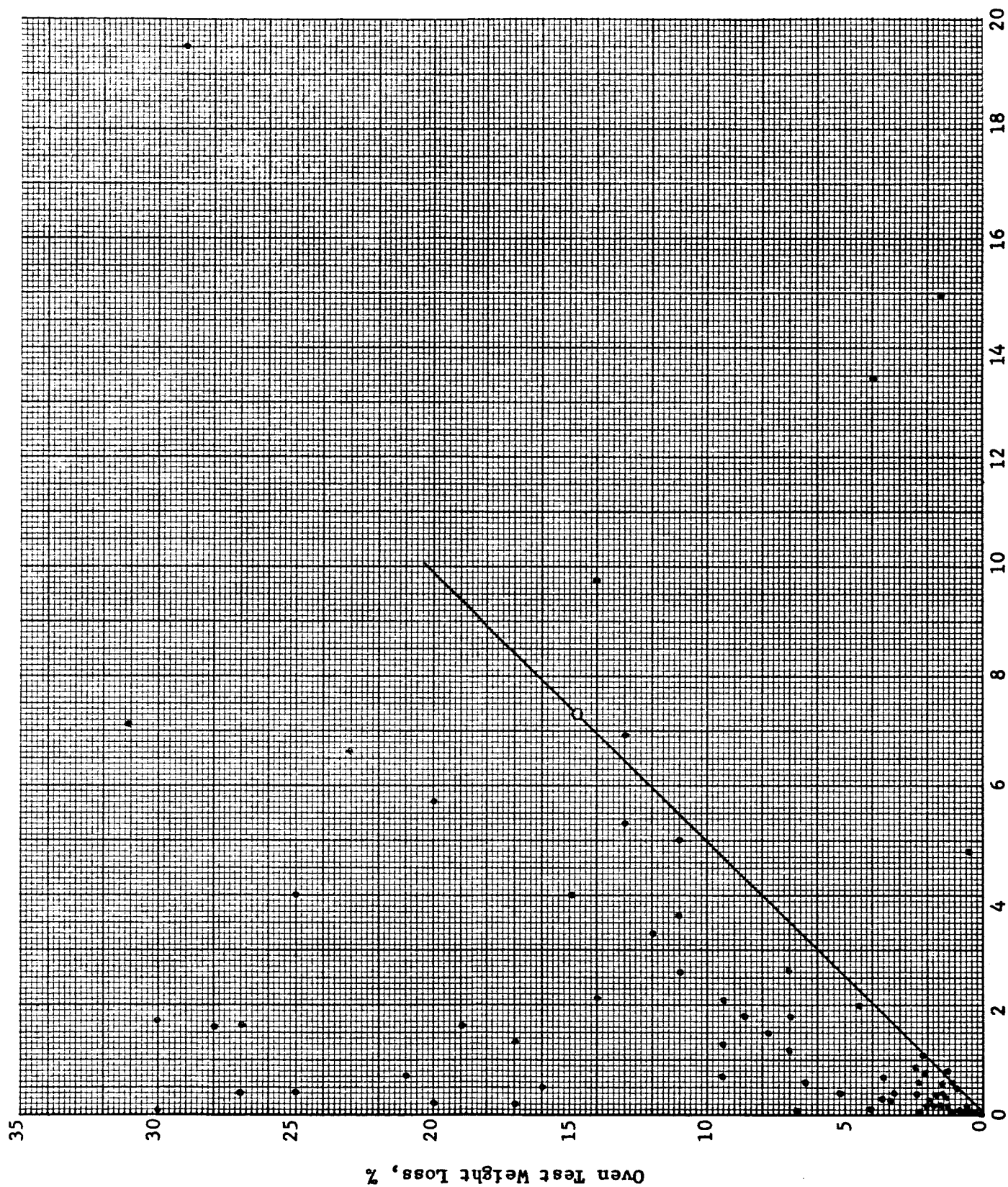


FIGURE 3 COMPARATIVE WEIGHT LOSS DATA FOR OVEN TEST (350°F) AND SCREENING TEST (200°F)

Gassing Rates for Materials in
Stabilization and Control System

Time-Line Analysis of Gassing Rates for SCS

A time-line analysis of gassing rates for the SCS was based on a power profile for its subsystems and a listing of organic material weights by subsystem. A modified power profile, Table 2, presents the fraction of full power at which each of the 13 subsystems operates at any time during a 14-day lunar mission. This table includes some arbitrary selections of maximum power, and some "smoothing" of power inputs by a time-weighted average where the power profiles were jagged. The abbreviated profile is more than adequate in consideration of the modest fluctuation in power level with time.

The abbreviated power profile was used to project material temperatures. All organic materials within a subsystem were arbitrarily considered to be at 150°F whenever that subsystem was operating at maximum power, or at 80°F when that subsystem was operating at zero power. For intermediate power levels, it was assumed that the weight of material at 150°F is proportional to the power level expressed as fraction of full power for the subsystem concerned. Accordingly, the material inventory of the SCS was distributed among the subsystems (Table 3) and used to calculate weights of material at 150°F in each subsystem at any time (Table 4). The balance of the weight of each material could be considered to be at 80°F. For ease of calculation,

TABLE 2
MODIFIED POWER PROFILE FOR SCS*

Time Hours	Subsystem												
	1	2	3	4	5	6	7	8	9	10	11	12	13
1	1.0	1.0	1.0	1.0	1.0	0.0	1.0	1.0	0.0	0.21	1.0	1.0	1.0
6	0.725									0.79			0.12 avg.
12										0.62			
13	1.0												0.06
45	0.725												1.0
46													0.00
51										1.0			1.0
79													0.0
80	1.0									0.62			1.0
86	0.725									1.0			0.0
112	1.0									0.62			1.0
120	0.725									0.62			0.0
130	1.0									1.0			1.0
131	0.725									0.62			0.0
166	1.0									1.0			1.0
172	0.725									0.62			0.0
178	1.0									1.0			1.0
182	0.725									0.62			0.0
246	1.0									1.0			1.0
250	0.725									0.62			0.0
267	1.0									1.0			1.0
268	0.725									0.62			0.0
326	1.0									1.0			1.0
327	0.725									0.62			0.06
333	1.0												0.014
336	1.0									0.62			0.3

*Entries are fractions of maximum power level for each subsystem.

TABLE 3

MATERIAL INVENTORY OF SCS, AND DISTRIBUTION OF
MATERIALS (IN GRAMS) AMONG SUBSYSTEMS

Material		Subsystem													
Name	Spec. No.	1	2	3	4	5	6	7	8	9	10	11	12	13	Total
Glass-Epoxy Laminate	6473	299		126.1				228.4	63.7				12.24	17.5	747
Epoxy Varnish	7134B	53.4	32.9		37.5		29.8	33.6						0.69	188
Fiberglass Tape	6771													6.57	6.6
Lubricant	6762					0.48	0.9					9.92	0.84	2.25	14.4
Silicone Rubber	7147A	54.1	83.3		82.5			80.5						1.14	302
Polyester Enamel	7664						17.5		14.6	6.8	12.2		9.73	5.59	66.4
Epoxy-Glass Laminate	7560		260.4		228.4						110	345.6			944
Nylon Tying Cord	7022					36.1					26.8		4.15		67
Polyester Tape	6856									17.8	0.5				34.7
Epoxy Adhesive	6020G		915.3									10.73			926
Silicone Adhesive	7228											15.09			15.1
Urethane Foam	7616											34.14			34.1
Acrylic	6025											0.33			0.33
Rubber Adhesive	6733					1.9		72.8				2.83			339
Epoxy Foam	7609	95.7	93.8		71.7			869.1							3870
Photographic Film	7570	1383.8			830.3		12.4								12.4
Marking Ink	7765		0.22												0.44
Acrylic Enamel	7541									4.2					4.2
Viton A	7159						12.6								12.6

TABLE 4

ESTIMATED WEIGHTS OF MATERIALS IN SCS AT 150°F VERSUS MISSION TIME

Time, Hours	Material																		
	6473	7134B	6771	6762	7147A	7664	7560	7022	6856	6020G	7228	7616	6025	6733	7609	7570	7765	7541	7159
1	747	158	6.6	13.5	302	32.5	857	45.9	16.4	926	15.1	34.1	0.33	340	3870	12.4	0.44	0	0
6	747	158	6.6	13.5	302	39.5	921	61.7	"	"	"	"	"	340	3870	"	"	"	"
12	665	143	6.6	13.5	287	39.5	921	61.7	"	"	"	"	"	312	3500	"	"	"	"
13	650	143	0.7	11.5	287	32.6	902	56.9	"	"	"	"	"	312	3500	"	"	"	"
45	732	157	0.7	11.5	301	32.6	902	56.9	"	"	"	"	"	340	3870	"	"	"	"
46	650	143	0.7	11.2	286	32.6	902	56.9	"	"	"	"	"	312	3500	"	"	"	"
51	648	143	0.4	11.2	286	32.2	902	56.9	"	"	"	"	"	312	3500	"	"	"	"
79	648	143	0.4	11.2	286	36.8	944	61.7	"	"	"	"	"	312	3500	"	"	"	"
80	747	158	6.6	13.5	302	42.1	944	61.7	"	"	"	"	"	340	3870	"	"	"	"
86	648	143	0.00	11.2	286	31.9	902	56.9	"	"	"	"	"	312	3500	"	"	"	"
112	747	158	6.6	13.5	302	42.1	944	67.0	"	"	"	"	"	340	3870	"	"	"	"
120	648	143	0.00	11.2	286	31.9	902	56.9	"	"	"	"	"	312	3500	"	"	"	"
130	747	158	6.6	13.5	302	42.1	944	67.0	"	"	"	"	"	340	3870	"	"	"	"
131	648	143	0.00	11.2	286	31.9	902	56.9	"	"	"	"	"	312	3500	"	"	"	"
166	747	158	6.6	13.5	302	42.1	944	67.0	"	"	"	"	"	340	3870	"	"	"	"
172	648	143	0.00	11.2	286	31.9	902	56.9	"	"	"	"	"	312	3500	"	"	"	"
178	747	158	6.6	13.5	302	42.1	944	67.0	"	"	"	"	"	340	3870	"	"	"	"
182	648	143	0.00	11.2	286	31.9	902	56.9	"	"	"	"	"	312	3500	"	"	"	"
246	747	158	6.6	13.5	302	42.1	944	67.0	"	"	"	"	"	340	3870	"	"	"	"
250	649	143	0.4	11.4	286	32.2	902	56.9	"	"	"	"	"	312	3500	"	"	"	"
267	731	157	0.4	11.4	286	32.2	902	56.9	"	"	"	"	"	340	3870	"	"	"	"
268	648	143	0.1	11.2	286	32	902	56.9	"	"	"	"	"	312	3500	"	"	"	"
326	735	157	2.0	11.5	302	33.6	902	56.9	"	"	"	"	"	340	3870	"	"	"	"
327	653	143	2.0	11.5	286	33.6	902	56.9	"	"	"	"	"	312	3500	"	"	"	"
333	747	158	6.6	13.5	302	37.5	902	56.9	"	"	"	"	"	340	3870	"	"	"	"
336	747	158	6.6	13.5	302	37.5	902	56.9	"	"	"	"	"	340	3870	"	"	"	"

these latter weights were converted by a factor of 8.15 to corresponding weights which would gas at the same rate at 150°F in order to obtain the final temperature profile of Table 5.

From Table 5, generation rates may be correlated with individual materials or with the total system. It should be noted that the time-temperature profile indicates only small fluctuations of generation rate with time. The time-weighted averages of the weights of each material at 150°F can be used to estimate trace material generation rates.

TABLE 5

"TEMPERATURE PROFILE" FOR MATERIALS IN SCS. GRAMS AT 150°F*

Time, Hours	Material														
	6473	7134B	6771	6762	7147A	7664	7560	7022	6856	6020G	7228	7616	6025	6733	7609
1	747	162	6.6	13.6	302	36.7	868	48.5	18.6	926	15.1	34.1	0.33	340	3870
6	747	162	6.6	13.6	302	42.8	924	62.4	18.6	"	"	"	"	340	3870
12	675	149	6.6	13.6	289	42.8	924	62.4	18.6	"	"	"	"	315	3545
13	662	149	1.3	11.9	289	36.8	907	58.1	18.6	"	"	"	"	315	3545
45	734	161	1.3	11.9	301	36.8	907	58.1	"	"	"	"	"	340	3870
46	662	149	1.3	11.6	288	36.8	907	58.1	"	"	"	"	"	315	3545
51	660	149	0.45	11.6	288	36.4	907	58.1	"	"	"	"	"	315	3545
79	660	149	0.45	11.6	288	40.4	944	62.4	"	"	"	"	"	315	3545
80	747	162	6.6	13.6	302	45.1	944	62.4	"	"	"	"	"	340	3870
86	660	149	0.8	11.6	288	36.1	907	58.1	"	"	"	"	"	315	3545
112	747	162	6.6	13.6	302	45.1	944	67.0	"	"	"	"	"	340	3870
120	660	149	0.8	11.6	288	36.1	907	58.1	"	"	"	"	"	315	3545
130	747	162	6.6	13.6	302	45.1	944	67.0	"	"	"	"	"	340	3870
131	660	149	0.8	11.6	288	36.1	907	58.1	"	"	"	"	"	315	3545
166	747	162	6.6	13.6	302	45.1	944	67.0	"	"	"	"	"	340	3870
172	660	149	0.8	11.6	288	36.1	907	58.1	"	"	"	"	"	315	3545
178	747	162	6.6	13.6	302	45.1	944	67.0	"	"	"	"	"	340	3870
182	660	149	0.8	11.6	288	36.1	907	58.1	"	"	"	"	"	315	3545
246	747	162	6.6	13.6	302	45.1	944	67.0	"	"	"	"	"	340	3870
250	660	149	0.45	11.8	288	36.4	905	58.1	"	"	"	"	"	315	3545
267	733	161	0.45	11.8	288	36.4	905	58.1	"	"	"	"	"	340	3870
268	660	149	0.9	11.6	288	36.2	905	58.1	"	"	"	"	"	315	3545
326	737	161	2.6	11.9	302	37.6	905	58.1	"	"	"	"	"	340	3870
327	665	149	2.6	11.9	288	37.6	905	58.1	"	"	"	"	"	315	3545
333	747	162	6.6	13.6	302	41.1	905	58.1	"	"	"	"	"	340	3870
336	747	162	6.6	13.6	302	41.1	907	58.1	"	"	"	"	"	340	3870
Time- Weighted Average 673	151	1.64	11.9	290	37.3	910	58.7	18.6	926	15.1	34.1	0.33	318.5	3590	12.4
														0.515	1.6

*Entries are reported as fictitious weights in grams of each material considered as being at 150°F for purposes of calculating gassing rates.

Generation Rate Profile for SCS

Equation [1] was employed to extrapolate weight loss data on the SCS to an operational period of 14 days; a period of 1000 hours, assumed as an average for operational running of all systems before launch (Table 1), was taken into account. The extrapolated weight losses were apportioned between carbon monoxide and total organics for each material (Table 6) using gas identification data from Honeywell's report to North American Aviation (NAA)⁽²⁾. The total organic output of each material was further apportioned among the specific identified and unknown compounds according to relative concentrations of organic contaminants as found in the same study for NAA (Table 7). Trace contaminants were summed over all materials in the inventory to provide a listing of amounts of 12 specific organic compounds and of a group of unknowns (Table 8).

TABLE 6

GENERATION RATES OF CARBON MONOXIDE AND TOTAL ORGANICS
FOR SCS DURING PERIOD OF 40 TO 54 DAYS

Material	Specification	Weight Material,* g	Quantities of Trace Materials			
			CO g x 10 ³	CO Micromoles	Total Org. g x 10 ³	Total Org. Micromoles
Glass Epoxy Laminate	6473	673.	4.54	162.	35.7	496.
Epoxy Varnish	7134B	151.	2.36	84.3	137.	1905.
Fiberglass Tape	6771	1.64	0.0051	0.18	0.030	0.42
Lubricant	6762	11.9	0.0	0.0	3.0 est.**	<42. est.**
Silicone Rubber	7147A	290.	0.0	0.0	6.7	93.4
Polyester Enamel	7664	37.3	1.07	38.4	2.9	40.6
Epoxy Glass Laminate	7560	910.	<10.	<140.	<2.3	<320.
Nylon Tying Cord	7022	58.7	0.0	0.0	51.7	718.
Polyester Tape	6856	18.6	1.45	51.8	11.1	155.
Epoxy Adhesive	6020G	926.	19. est.**	680. est.	10. est.	142. est.
Silicone Adhesive	7228	15.1	0.0	0.0	1.4	19.6
Urethane Foam	7616	34.1	0.0	0.0	12.0	167.
Acrylic	6025	0.33	0.0071	0.253	0.039	0.54
Rubber Adhesive	6733	318.5	0.0	0.0 est.	<260. est.	<3600. est.
Epoxy Foam	7609	3590.	120.6	4307.	565. est.	7850. est.
Photographic Film	7570	12.4	0.0	0.0	<0.08 est.	<1.0 est.
Marking Ink	7765	0.44	0.0 est.	0.0 est.	0.0 est.	0.0 est.
Acrylic Enamel	7541	0.51	<0.004 est.	<0.05 est.	<3.7 est.	<51. est.
Viton A	7159	1.6	0.021	0.75	<0.27 est.	<3.7

* These are actual weights corrected on the basis of the power profile for the mission to equivalent weights at 150°F.

**Estimated values arise where accuracy of data are in question or when data are based on gassing results at 200°F. rather than on oven test data at 350°F.

AMOUNTS AND DISTRIBUTION OF TRACE CONTAM

Material	CO, Micromoles	Total Organic Micromoles	Amount of Org				
			AC	MEK	EAL	MIBK	TOL
6473	162.1	496	60 (0.12)	50 (0.1)	100 (0.2)	100 (0.2)	20 (0.04)
7134B	84.3	1905	419 (0.22)			724 (0.38)	
6771	0.2	0.4	0.25 (0.63)				
6762	0	<42					
7147	0	93.4			93 (1.0)		
7664	38.4	40.6					
7560	<140	<320					105 (0.33)
7022	0	718					
6856	51.8	155	93 (0.6)				
6020G	680	142					
7228	0	19.6			10 (0.56)		
7616	0	167	137 (1.0)				
6025	0.25	0.5					
6733	0	<3600	2400 (0.67)	40 (0.01)		220 (0.06)	540 (0.15)
7609	4307	7850					
7570	0	<1.0	0.14 (0.14)			0.09 (0.09)	
7541	<0.05	<51					7 (0.14)
7159	<0.75	<3.7					
TOTALS	5465	15,555	3109	90	203	1044	672

25①

BLE 7

NANTS FROM MATERIALS IN SCS (14-DAY MISSION)

nic Trace Contaminants, Micromoles (Mole Fraction)

EBE	XYL	NBAL	MMC	IPAL	HEP	CUM	UNK
95 (0.05)	629 (0.33)	125 (0.25)	40 (0.08)	0.15 (0.37)			38 (0.02)
	14 (0.35)	9 (0.21)				105 (0.33)	18 (0.44) 110 (0.34) 718 (1.0) 62 (0.4) 10 (0.44)
	40 (0.01)		0.5 (1.0)	140 (0.04) 7370 (0.94)	480 (0.06)		220 (0.06) 0.62 (0.62) 3.7 (1.0)
7 (0.14)	0.09 (0.09) 37 (0.72)	0.06 (0.06)					
102	720	134	40	7510	480	105	1180

25 (2)

TABLE 8

TRACE CONTAMINANTS FROM SCS
DURING 14-DAY MISSION

<u>Trace Material</u>	<u>Symbol</u>	<u>Amount</u> <u>Micromoles</u>
i-Propyl Alcohol	IPAL	7,510
Carbon Monoxide	CO	5,465
*	AC	3,109
Methyl-n-Butyl Ketone	MIBK	1,044
o-m- or p-Xylene	XYL	720
Toluene	TOL	672
Heptane	HEP	480
Ethyl Alcohol	EAL	203
n-Butyl Alcohol	NBAL	134
Cumene	CUM	105
Ethyl Benzene	EBE	102
Methyl Ethyl Ketone	MEK	90
Methyl Methacrylate	MMC	40
Unknowns	UNK	1,180

*Acetone, ethyl formate and/or methyl acetate.

Trace Materials not Generated by Stabilization
and Control System

Honeywell's thorough inventory of the SCS permitted a detailed study of its trace material generation rate profile. No inventory was available for other systems. It was proposed, therefore, to estimate the total generation rate profile for all materials and equipment by some type of extrapolation of data for the SCS. Studies of the atmosphere of Mercury capsules provide the clue for useful extrapolation.

Some of the trace materials known to arise from the SCS were found in Mercury capsule atmospheres. New trace materials found in Mercury capsule atmospheres, but not generated by materials in the SCS, are assumed to arise from other systems than the SCS. Accordingly, it was possible to develop proportionality factors for trace material generation rates in the SCS to account for the contributions of other materials and equipment.

To illustrate the above reasoning, consider the fairly constant proportionality among concentrations of the same materials found in both Apollo SCS and Mercury capsule atmospheres.

<u>Material Pair</u>	<u>Average Concentration Ratio</u>	
	<u>Mercury</u>	<u>Apollo SCS</u>
TOL/EAL	7.55	3.3
EAL/MEK	3	2.3
TOL/NBAL	5.75	4.9

One can presume that equipment on Apollo C/M will introduce trace materials not found in the SCS roughly in proportions found for Mercury atmospheres.

The new materials always found in Mercury atmospheres are Freon 114, vinylidene chloride, methylene chloride, and benzene. Ethylene dichloride was found sometimes, and should be considered here because of its high toxicity and the likelihood of its being present in substantial amount. The relative amounts of these new materials and of one material (ethyl alcohol) common to both atmospheres are as follows:

<u>Trace Material</u>		<u>Maximum Amount from Mercury Tests, ppm</u>
<u>Name</u>	<u>Symbol</u>	
Freon 114	F114	6,000
Ethylene Dichloride	EDC	40
Vinylidene Chloride	VDC	2
Methylene Chloride	MC	2
Benzene	BEN	1
Ethyl Alcohol	EAL	3

Trace materials common to both atmospheres are present at roughly a three-fold higher concentration in the Mercury capsule atmosphere than in the Apollo C/M atmosphere on the basis of the SCS contribution to trace material generation. Therefore, it is estimated that there will be approximately three times more electronic gear than represented by the SCS contributing to trace material contamination. Accordingly, the generation rate profile of Table 7 can be multiplied by three and the new trace materials may be added to the list in the proportion found in Mercury capsule atmospheres. This provides the complete rate generation pattern for materials, processes, and equipment.

Specifically, the amount of ethyl alcohol from Table 7 is 203 micro-moles. If the total amount of alcohol is three times this value, the amounts of new materials are as reported in Table 9.

TABLE 9

AMOUNTS OF TRACE CONTAMINANTS GENERATED BY OTHER THAN
ELECTRONIC GEAR (14-DAY MISSION)

<u>Trace Contaminant</u>	<u>Relative Amount</u>	<u>Actual Amount, Micromoles</u>
F114	6,000	1,218,000
EDC	40	8,120
VDC	2	406
MC	2	406
BEN	1	203
EAL	2	609

Volatile Materials of Biological Origin

In assessing the identity and amount of volatile materials to be expected from biological sources, considerable reliance has been placed on secondary sources of information such as texts, the Bioastronautics Data Book, and the Biology Data Book. Efforts have, however, been made to search out significant additions to the literature which have appeared since 1960, and to return to the original literature to evaluate particularly important conclusions.

Sources of atmospheric contamination considered, and disposition made of the sources are tabulated in Table 10.

TABLE 10

DISPOSITION OF BIOLOGICAL SOURCES OF ATMOSPHERIC CONTAMINATION

<u>Source</u>	<u>Disposition</u>
Feces	Not considered a significant source of atmospheric contamination since feces are to be deposited in a gas-proof bag which is immediately sealed.
Urine	Same as for feces.
Skin Secretions	It is assumed that all skin secretions, including sweat and sebum, reach the space capsule atmosphere except as limited by their volatility.
Intestinal Gases	Assumed that all flatus gases reach the atmosphere of the space capsule.
Breath	Assumed that all respiratory gases reach the space capsule atmosphere.
Food	Since Food is to be packaged in hermetically sealed containers to be opened only as the food is consumed, it is assumed not to make significant contributions to the atmospheric contamination. Experience has shown that food odors can be noticeable with extremely small actual concentrations of odor components. The marked odors of many food items might suggest that significant contamination of the atmosphere with compounds from the food would occur even in the brief exposure to air that occurs when the packages of food are opened for consumption. Attempts to identify the flavor components of food, however, have served to emphasize the exquisite sensitivity of the olfactory apparatus. Ionization detectors, such as are used in gas chromatography, can detect parts per billion, but the olfactory nerves can detect 100 to 10,000 times less(30,31). The number of compounds actually involved in food odors have proved extremely numerous(32,33).
Hygiene Activities	Since these are to be limited to provisions for towel-ling, they are assumed to make no significant contri-butions.
Miscellaneous Sources	
Tears	None considered significant sources of atmospheric contamination.
Nasal Drippings	
Hair	
Nail Clippings	
Ear Wax	

In estimating atmospheric contributions, an effort has been made to keep the estimates within what seem reasonable ranges, but to tend toward high rather than low estimates. This is, of course, in the interest of safety. All rate estimates are on a per man basis.

Information is almost totally lacking in some areas, and this is pointed out in the discussion. In some cases, it is possible that a very extensive effort in searching the literature would supply additional useful data.

Skin Secretions

Skin secretions include eccrine sweat, apocrine sweat, and sebum. Added to these are materials contributed by sluffing of the surface layer of cells, and materials added by gas exchange through the skin. Finally, bacterial action may play an important part in altering the identity of the materials after they appear at the skin surface. The magnitude of these alterations will be dependent on body hygiene and the means taken to cope with actual runoff of sweat.

It is assumed that only volatility will limit the contribution of skin secretions to the atmosphere. This is, of course, an extreme assumption, conservative on the side of safety. If skin secretions are physically removed and disposed of, they will to that extent not make contributions to the atmosphere. Skin secretions which are absorbed on clothing may or may not continue to make atmospheric contributions, depending on the disposition that

is made of the clothing. The wearing of light clothing may not markedly reduce the amount of volatile skin secretions escaping into the atmosphere. As the clothing becomes saturated, it presents a large surface for evaporation.

Eccrine Sweat. Eccrine sweat is that part of the total skin secretions contributed by thermally responsive sweat glands. These are unevenly distributed over the body surface, there being about six times the density of sweat glands on the palms of the hands as on the back and buttocks. The composition of eccrine sweat is not constant, but is, among other influences, a function of the sweating rate. Rothman⁽³⁾, for example, notes nitrogen concentrations of 68 mg per 100 cc in profusely emitted sweat and 275 mg per 100 cc in intermittently secreted sweat. These effects are at least in the direction of rendering total secretion of solutes less dependent of sweat volume.

Measurements of sweat composition have frequently been made by surrounding a body member with an impermeable bag and collecting all aqueous secretions for analysis. Other collection techniques have sometimes been used. Accordingly, measurements of sweating rate are subject to wide variation, and values from near zero to over three liters per hour have been noted. The recent data of Consolazio and co-workers⁽⁴⁾ seem a good basis on which to make estimates for present purposes. He conducted studies at a series of temperatures and for an activity profile in which most of the day was spent

in sedentary activity except for two exercise periods of 50 minutes each.

Sweating rates were:

Mean Temp., °F	Sweat Rate g/hr
70	143
85	242
100	312

Using these values together with values cited in the Bioastronautics Data Book⁽⁵⁾, the following sweating rates have been selected as a basis for calculation of atmospheric contamination from sweat:

Low	50 g/hr
Median	250 g/hr
High	400 g/hr

The median value is used in calculating the amounts of individual trace materials discussed below.

Lactic Acid. Lactic acid appears in sweat in relatively large amounts and has significant volatility. It must, therefore, be considered a potential contaminant. The amount in sweat has been shown by Astrand⁽⁶⁾ to go as high as 500 mg per 100 ml during the first of a sweating period, but to level off at about 156 to 190 mg per 100 ml as sweating continues. Using 190 mg per 100 ml for purposes of calculation and using sweating rates calculated above, the total lactate secretion might be:

Low	95 mg/hr
Median	475 mg/hr
High	760 mg/hr

The total amount of this supply which will evaporate into the atmosphere is limited by the amount present as lactic acid itself, by the concentration reached as the water component of sweat evaporates, by the temperature, and by the surface area from which evaporation occurs.

The amount present as lactic acid is a function of pH. Skin pH values do not ordinarily vary by more than one pH unit and pH 5.7 represents a good estimate of the mean. At pH 5.7 most of the lactic acid will be present as the lactate ion, since the ionization constant of lactic acid is 1.5×10^{-4} ($pK_a = 3.81$). Only about one percent of the lactic acid will be present in nonionized form at pH 5.7, and only about 10 percent at pH 4.7. The vapor pressure of pure lactic acid at 40°C would be about 0.25 mm. This means that at equilibrium the air above lactic acid at 40° will contain 1.4×10^{-4} mole per liter.

If nearly all the aqueous phase of sweat evaporates it could leave behind a system containing lactic acid and lactates. Limiting concentrations of lactic acid will then be:

at pH 4.7 - 14μ mole/l gas
at pH 5.7 - 1.4μ mole/l gas

If new sweat accumulates so that the limiting concentration on the evaporative surface is 1 m, then the mole fraction of total lactate will be about 0.02 and the limiting concentrations will be:

at pH 4.7 - 0.28μ mole/l gas
at pH 5.7 - 0.028μ mole/l gas

The latter conditions seem the likely ones, and a limiting concentration of 0.05μ mole per liter of atmosphere seems a safe estimate.

It is instructive to estimate the probable rate of evaporation of free lactic acid should it by chance be present in greater amounts than indicated above. This was done by noting the constant proportionality between measured rates of evaporation and vapor pressures for the case of water (Figure 4) down to the ice point. If evaporation rate is proportional to vapor pressure, and if the latter declines exponentially with decreasing temperature, it is apparent that the evaporation rate of slightly volatile acids will be very low at body temperature. For the case of lactic acid having a vapor pressure of two mm Hg at 57°C , the evaporation rate would be about one g per square foot per hour. This is the rate of evaporation of water having a vapor pressure of two mm Hg. At body temperature, the vapor pressure of lactic acid would be near 0.25 mm Hg. The corresponding evaporation rate would be near 0.06 g per square foot per hour or 1.2 g per man-hour as a maximum. In consideration of the fact that less than one percent of the acid is free acid, and that vapor pressure would be lowered by a factor of 50 for 0.02 mole fraction solution, this maximum rate would be reduced by a factor of about 4000 to 2.4×10^{-4} g per man-hour or 2.5μ moles per man-hour.

This is a borderline rate for atmospheric contamination. In view of the probability that there will be even less than one percent free lactic acid, this acid will not be given further consideration as a trace contaminant.

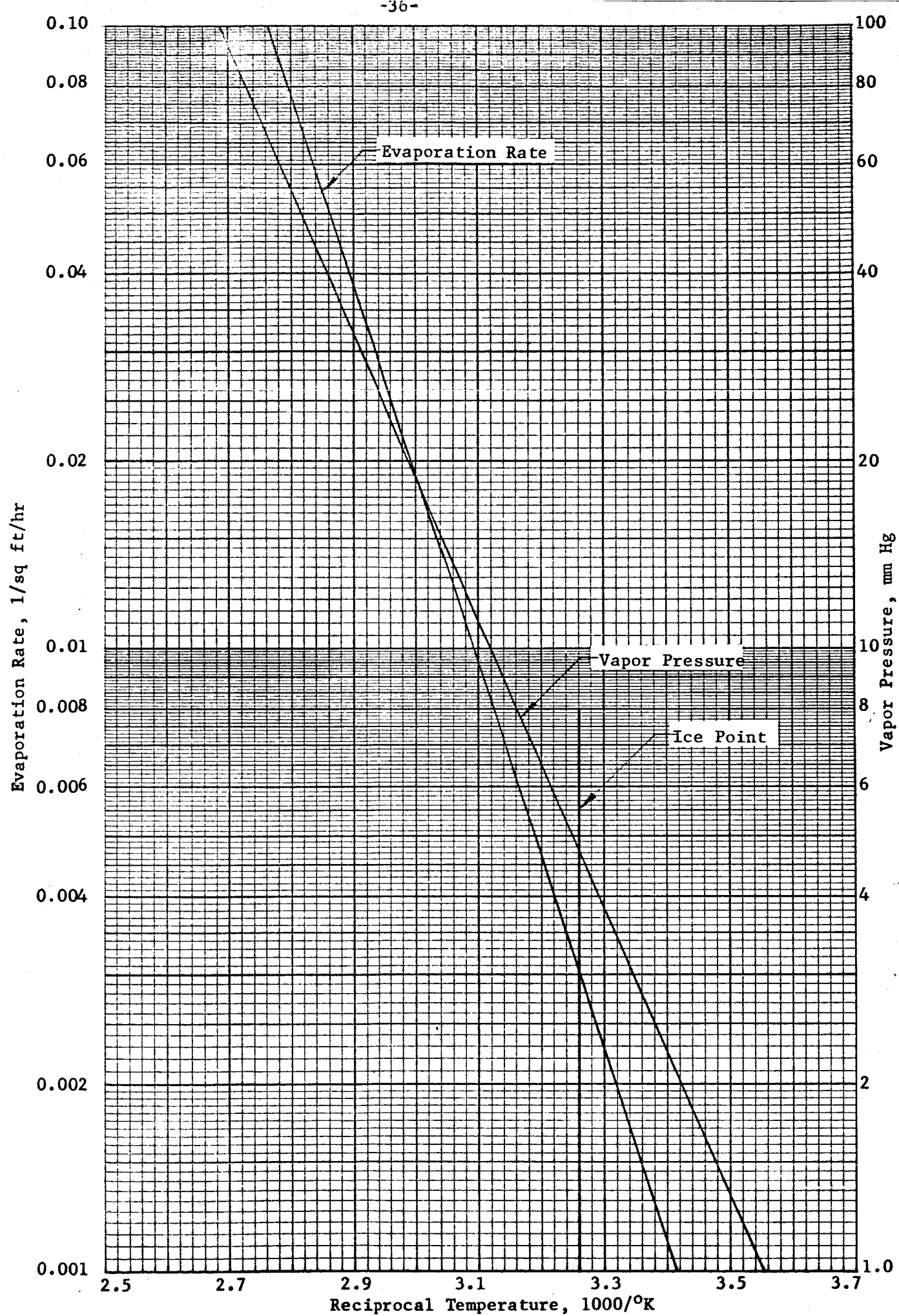


FIGURE 4 VAPOR PRESSURE AND EVAPORATION RATE FOR WATER

Ammonia. "Ammonia" is present in only minimal quantities in freshly excreted sweat⁽¹⁾. It is formed by bacterial decomposition of urea. The amount found on examination of sweat usually ranges from 2.5 to 35 mg per 100 ml⁽⁵⁾. If 20 mg per 100 ml is used for purposes of calculation, then estimates of amounts produced would be:

Low	10 mg/hr
Median	50 mg/hr
High	80 mg/hr

The actual concentration of ammonia as such will be a function of the pH of the system. The ionization constant of ammonium hydroxide is 2.5×10^{-5} at 40°C. The pH at the equivalence point will, therefore, be about 9.25. This means that at the pH prevailing on the skin (5.7) about 0.06 percent of the total ammonia of the system will be nonprotonated. The volatility will be limited by concentration and by pH shifts which occur as ammonia is lost from the system.

If evaporation of water occurs so rapidly that the skin remains essentially dry, then the contribution to the atmosphere might be estimated at less than the following values:

Low	$0.0006 \times 10 \text{ mg/hr} = 0.006 \text{ mg/hr} = 0.35\mu \text{ mole/hr}$
Median	$0.0006 \times 50 \text{ mg/hr} = 0.03 \text{ mg/hr} = 1.7\mu \text{ mole/hr}$
High	$0.0006 \times 80 \text{ mg/hr} = 0.048 \text{ mg/hr} = 2.8\mu \text{ mole/hr}$

Since the skin will nearly always be fairly moist, actual rates will be 0.1 to 0.0002 of these values. Rates of 0.02 μ mole per hour might represent a reasonable estimate.

These calculations assume that the anions are nonvolatile. This may not be entirely correct. Dissociation of weak salts to yield volatile acids and ammonia could raise these values somewhat.

Since ammonia at the body surface is largely contributed by urea decomposition, estimates of the potential supply are of some pertinence. It is possible that bacterial action on sweat-soaked clothes where the buffering action of new sweat deposits was not available might contribute substantial quantities of ammonia. The amount of urea in sweat expressed in terms of urea nitrogen is given as 5 to 39 mg per 100 ml by Bioastronautics Data Book⁽⁵⁾. A paper by Brusilow and Gordes⁽⁷⁾ gives data covering the range 13.5 to 40 mg per 100 ml.

If 30 mg of potential ammonia per 100 ml sweat is used for purposes of calculation, estimates of rates become:

Low	15 mg/hr = 0.89 m mole/hr
Median	75 mg/hr = 4.2 m mole/hr
High	120 mg/hr = 7.0 m mole/hr

Phenol. The amount of phenol in sweat is given in the Bioastronautics Data Book⁽⁵⁾ as two to eight mg per 100 ml of sweat. The source of these data is apparently Altman and Dittmer⁽⁸⁾. Altman and Dittmer

reference their source incorrectly, but do list in their references a source which refers in turn to a paper by Deichmann and Schafer⁽⁹⁾. These workers found 0.09 to 0.44 mg of free phenol and 0.04 to 0.11 mg of conjugated phenol per 100 ml of sweat. Total concentrations were from 0.16 to 0.55 mg per 100 ml. These values are an order of magnitude lower than those cited by Altman and Dittmer.

Using 0.4 mg per 100 ml for making estimates of phenol from sweat one obtains the following figures:

Rate = 0.4 mg/100 ml

Low	0.2 mg/hr = 2.1 μ mole/hr
Median	1.0 mg/hr = 10 μ mole/hr
High	1.6 mg/hr = 17 μ mole/hr

Phenol has a vapor pressure of one mm Hg at 40°C. Moreover, the water-phenol system shows positive deviations from ideality, thus leading to effective removal of phenol by aeration, or distillation. It is, therefore, expected that phenol will be evaporated along with sweat. The figure of 10 μ mole per man-hour is used for calculation of contamination rates.

Iodine. Iodide ion is a potentially volatile material since it may be gradually oxidized to iodine by exposure to atmospheric oxygen. The total amount available is, however, judged too small to be of importance. The concentration in mg per 100 mg sweat is given as 0.0009⁽⁵⁾. At the median sweating rate of 250 ml per hour, this would give only 2 mg per three-man mission of 14 days.

Apocrine Sweat. Apocrine sweat is produced by glands located in the axillae, perimamillary regions, mid-line of the abdomen, mons pubis, perigenital, and perineal areas and in the external ear, and the nasal vestibulae. These glands do not respond to thermal stimulation but do respond to mental stimuli via the adrenergic system⁽³⁾. Data on the composition of apocrine sweat are minimal. Rothman⁽³⁾ states that free fatty acids are present even in the absence of bacterial action. Limited data gathered by Thurmon and Ottenstein⁽¹⁰⁾ indicate pH values about one-half unit higher than eccrine sweat, and lactate concentrations about equivalent to eccrine sweat. Ottenstein⁽¹¹⁾ gives figures indicating ammonia levels several times higher than for eccrine sweat but with lower urea values. One suspects bacterial action.

Kligman and Shebackh⁽¹²⁾ report that apocrine sweat becomes odorous only as a result of bacterial action. They also report the apocrine glands of pubic regions to be nonfunctional.

From the limited data available one might expect that the apocrine sweat would contribute principally to additional ammonia, probably to the extent of 0.05 μ mole per hour. This is negligible compared to the amount produced by bacterial action.

Insensible Sweat. Insensible sweat arises by unnoted evaporation of eccrine and apocrine sweat, and by water exchange directly through the skin. Methodology used to measure total sweat would include the volatile components of insensible sweat within the resulting estimates.

Sebum. Sebum consists of fat and cellular debris on the skin surface. A main source is the sebaceous glands associated with hair follicles, present in man everywhere hair follicles are present. Other sources are apocrine glands and the keratinizing epidermis. Analytical examination has usually been confined to the lipid fraction. The amount of sebum produced is limited by the amount already present on the skin and by the temperature. Sebum tends to solidify in the gland openings and prevent further secretion until it is removed by physical means or by emulsification in sweat⁽¹³⁾. One is, therefore, concerned both with saturation levels and with rates of production. As in the case of sweat, material absorbed on clothing continues to be available for evaporation. The melting point of sebum is in the vicinity of 30°C⁽¹³⁾.

Saturation levels of sebum, where precautions to prevent removal are taken, have been reported at from 0.38 mg per sq cm to 3.38 mg per sq cm, with more of the values at the upper part of the range⁽³⁾. Levels observed without precautions to prevent removal have varied from 0.14 to 0.24 mg per sq cm^(14,15). These values are all based on measurements on the forehead. Values for other parts of the body may be only one-fifth as great. Some data cited by Carruthers⁽¹⁴⁾ are:

Forehead	2.44 mg/cm ²	
Vertebrae line	1.45 mg/cm ²	} Upper back
Nudiapsular lines	0.79 mg/cm ²	
Vertebrae line	0.75 mg/cm ²	} Lower back
Nudiapsular line	0.50 mg/cm ²	

Some production rates available in the literature are:

$$1.69 \pm 0.52 \text{ mg}/10 \text{ cm}^2/\text{hr} = 0.054 \text{ mg}/\text{cm}^2/\text{hr}, (15)$$

$$0.3 \text{ to } 1.8 \text{ mg}/20 \text{ cm}^2/\text{hr} = 0.015 \text{ to } 0.09 \text{ mg}/\text{cm}^2/\text{hr}, (13)$$

$$\text{and } 0.05 \text{ mg}/\text{cm}^2/\text{hr}. (14)$$

Minimum rate

$$0.1 \text{ } \mu\text{g}/\text{cm}^2/\text{min} = 0.006 \text{ mg}/\text{cm}^2/\text{hr} (3)$$

From these various considerations the following are estimated for purposes of calculation:

Casual levels

Low	0.15 mg/cm^2
Median	0.3 mg/cm^2
High	0.9 mg/cm^2

Production rates

Low	0.01 $\text{mg}/\text{cm}^2/\text{hr}$
Median	0.02 $\text{mg}/\text{cm}^2/\text{hr}$
High	0.05 $\text{mg}/\text{cm}^2/\text{hr}$

Lower Fatty Acids in Sebum. Butyric, valeric, and caproic acids are reported to be present in skin secretions to the extent of 1.2 percent. (5)

This estimate seems extremely doubtful. The source from which it comes (16) quotes the chemical analysis of sebum as:

Water	31.7 percent
Epithelium and protein	61.75 percent
Fat	4.16 percent
Butyric, valeric, and caproic acids	1.21 percent
Ash	1.18 percent

The methods of sebum examination usually used^(17,18) begin with organic-solvent extractions to remove the lipid, followed by examination of the materials so obtained. If butyric, valeric, and caproic acids were really present in large amounts, one would expect them to be extremely prominent in such extracts. Haahti,⁽¹⁷⁾ using careful gas chromatographic techniques, noted only traces of acids below C₁₂. Boughton and Wheatly,⁽¹⁸⁾ using gas chromatographic methods, placed the amount of fatty acids of C₁₀ and lower at 0.2 percent. If these acids are really present in large amounts, one would expect their salts to be leached into eccrine sweat, but they have not appeared prominently in analysis of this material.

The data giving butyric, valeric, and caproic acids as 1.2 percent of total skin secretions comes from Sunderman⁽¹⁶⁾ as a tertiary source. He identifies the original source as a 1912 text.⁽¹⁹⁾

Only traces of fatty acids C₇ to C₉ are present in sebum; the amounts are individually less than 0.05 percent.⁽¹⁴⁾

Data quoted by Carruthers⁽¹⁴⁾ give the amount of n-decanoic acid as 0.08 percent of the total free fatty acids of sebum in one case, and the total amount of free C₁₀ acids as 0.3 percent of the total free fatty acids of sebum in another case. About 30 percent of the total weight of sebum is free fatty acids.^(14,20)

The total amount in sebum using assumptions previously quoted in the general discussion of sebum will be:

Low	$0.15 \text{ mg sebum/cm}^2 \times 19,000 \text{ cm}^2 \times 0.30 \times 0.003 = 2.5 \text{ mg}$
Median	5.0 mg
High	15 mg

The production rate is estimated as follows:

Low	$0.01 \text{ mg/cm}^2/\text{hr} \times 19,000 \text{ cm}^2 \times 0.30 \times 0.003 = 0.17 \text{ mg/hr}$
Median	0.34 mg/hr
High	1.0 mg/hr

The actual amount reaching the atmosphere will be a function of its intrinsic volatility and its dilution by other components of the system. The vapor pressure of n-decanoic acid at 125°C is one mm Hg and at 268°C is 760 mm Hg. Extrapolation of the vapor pressure curve predicts a vapor pressure of only 0.01 mm at 37°C indicating a negligible evaporation rate. At one atmosphere pressure the limiting concentration is therefore one part by volume to 76,000 parts air or 80 ppm by weight. Since the acid makes up only about 0.09 percent of sebum and since the molecular weight of other components probably averages not more than three times that of decanoic acid, the limiting concentration can be estimated at

$$80 \text{ ppm} \times 0.0009 \times 3 = 0.21 \text{ ppm.}$$

This will be further reduced by the fact that the pH of skin will reduce the amount of nonionized fatty acid to about 15 percent of the total (pKa = 4.9).

It seems obvious that the contribution of decanoic acid will be negligible.

Higher Fatty Acids in Sebum. The percentage of total free fatty acids of sebum represented by the prominent higher members of the series is given by sources quoted in Carruthers⁽¹⁵⁾ as follows:

n-C ₁₂	3.6 percent
n-C ₁₄	6.3 percent
n-C ₁₆	24.2 percent
Oleic	35.6 percent

Data on the volatility of these acids follow:

Acid	Temperature, °C					
	<u>1 mm</u>	<u>10 mm</u>	<u>40 mm</u>	<u>100 mm</u>	<u>400 mm</u>	<u>760 mm</u>
n-C ₁₂	121	166	201	227	273	299
n-C ₁₄	142	199	223	250	294	318
n-C ₁₆	153	205	244	271	326	353
Oleic	176	223	257	286	334	360

Projecting these figures graphically, the vapor pressure of n-C₁₂ at 37°C is predicted at about 0.002 mm, and that of oleic acid at 0.00001 mm. Therefore, rates of evaporation would be negligible. The limiting concentration of pure lauric acid would be 0.000021 g per liter. At one atmosphere, this is 16 ppm. When the effects of concentration and of pH are taken into consideration, the equilibrium concentration is certainly not greater than 300 ppb. The equilibrium concentrations of the other acids considered in this group is still less.

Potential Fatty Acids in Sebum. The potential supply of fatty acids formed by hydrolysis of the glycerides of sebum would about double the free fatty acid fraction. Hydrolysis would free the acids of their chemical association with glycerin. However, the hydrolysis products probably would be buffered by ammonia and would not remain as free undissociated acid.

Flatus

Flatus will represent a major source of gaseous contamination of the space vehicle. The amount of flatus depends markedly upon the dietary composition, but those foods which promote flatus production are known, and it is assumed that they will be avoided in assembling the astronaut's diet. The composition of flatus varies markedly between individuals. It has been found that some people regularly produce hydrogen and others do not. Similarly, some persons produce methane and others do not. Murphy⁽²¹⁾ states that about half the subjects he has studied produce methane and half do not.

Flatus egestion is not constant, but periodic. Murphy⁽²¹⁾ estimates one 20-50 ml egestion per hour.

Some figures on flatus volume and composition are given in Table 11A.

TABLE 11

VOLUME AND COMPOSITION OF FLATUS

A. Volume Per Man

<u>Author</u>	<u>ml/Day</u>		<u>Base for Calculation</u>	<u>Reference</u>
	<u>Average</u>	<u>Range</u>		
Kirk	2140	520-5720	ml/min	22
Askevald	980	250-600	12-hr day ^(a)	23
			ml/min	23
Beazell, Ivy	527	380-655		24
Murphy		480-1200	"20-50 ml/hr"	21
		100-500		21

B. Methane in Flatus

<u>Author</u>	<u>Concentration, %</u>		<u>Estimated Rate of Production</u>	<u>Reference</u>
	<u>Average</u>	<u>Range</u>		
Kirk	7.2	0-30		22
Askevald	0.4 ± 0.1			23
Callaway			0-23 ml/hr	25
Murphy	18	0-40		21
Murphy			0-173 ml/day	26

C. Hydrogen in Flatus

<u>Author</u>	<u>Concentration, %</u>		<u>Estimated Rate of Production</u>	<u>Reference</u>
	<u>Average</u>	<u>Range</u>		
Kirk	20.9	3-34		22
Askevald	2.3 ± 0.5			23
Callaway			0-16 ml/hr	25
Murphy	9	0-50		21
Murphy			0-24 ml/day	26

^(a)Quoted range evidently for 12-hour day.

On the basis of these figures the following volume rates of production are used as a base for calculation:

Low	150 ml/day = 6.2 ml/hr
Median	600 ml/day = 25 ml/hr
High	1500 ml/day = 62 ml/hr

Methane. The amount of methane produced varies widely with individuals ranging from essentially none to several ml per hour. Some basis for estimates are given in Table 11-B.

Using Murphy's figure of 18 percent methane and applying it to volume estimates quoted earlier gives the following rates of production of methane:

Low	27 ml/day = 1.1 ml/hr
Median	108 ml/day = 4.5 ml/hr
High	270 ml/day = 11 ml/hr

These seem reasonable estimates in view of the data at hand.

It is to be remembered that the total methane addition to the atmosphere each hour may come in increments comprising the total hour's production, or even the production of several hours.

Hydrogen. The amount of hydrogen produced varies widely with individuals and may be none. Some basis for estimates are given in Table 11-C.

Using Murphy's figure of 9 percent average hydrogen in flatus and applying it to the volume estimates quoted earlier gives the following volume rates of production of hydrogen:

Low	13 ml/day = 0.54 ml/hr
Median	54 ml/day = 2.2 ml/hr
High	130 ml/day = 5.4 ml/hr

These seem reasonable estimates in view of the data available.

Hydrogen Sulfide. The amount of hydrogen sulfide in flatus has been inadequately determined. Kirk⁽²²⁾ gives an average value of 0.00028 percent on a cabbage-free diet. Murphy⁽²⁶⁾ has estimated the amount at certainly less than 0.0025 percent. Using the higher figure for safety estimates of generation rate are:

Low	0.0037 ml/day = 0.00015 ml/hr
Median	0.0150 ml/day = 0.00062 ml/hr
High	0.0370 ml/day = 0.0015 ml/hr

Unidentified Constituents. Murphy⁽²⁶⁾ has estimated unidentified constituents of flatus as being present in concentrations possibly as high as one percent.

Respiratory Gases

Hydrogen and methane occur in respiratory gases but as reflections of hydrogen and methane of flatus.⁽²⁶⁾ It is, therefore, probably not necessary that separate allowances be made for these gases from respiratory sources.

Because of the large volume of respiratory gases, the presence of even extremely small concentrations of materials in these gases could make very important contributions to air contamination in a closed space. The elimination of acetone in diabetes, of alcohol following ingestion, of ether and other organic solvents following administration, and of selenium-containing compounds by the respiratory route is well known. More attention to respiratory gases as a source of contamination would seem well warranted.

Carbon Monoxide. Carbon monoxide has been identified in expired air and hemoglobin breakdown has been incriminated as a source.⁽²⁷⁻⁹⁾ In three subjects the volume produced was estimated at 0.5, 0.65, and 1.05 ml per hour.⁽²⁹⁾ Concentrations in the expired air were from 0.00013 to 0.00017 percent. In a study of hospitalized subjects concentrations were 0.00023 ± 0.00001 percent.⁽²⁸⁾

Estimates for production per day might be:

Low	10 ml/day = 0.41 ml/hr
Median	20 ml/day = 0.84 ml/hr
High	30 ml/day = 1.2 ml/hr

Illness or infection might increase the amount.

Summary

Estimates of contributions to atmospheric contamination by materials considered in this literature search are summarized in Table 12. Converted to generation rates based on three men, these data represent the addition of new or additional trace contaminants in the amounts given in Table 13.

TABLE 12

PRODUCTION PER MAN OF ATMOSPHERIC CONTAMINANTS

<u>Substance</u>	<u>Source</u>	<u>Rate of Production*, μ Moles/Hour</u>			<u>Limiting Conc.**, μ Moles/l</u>
		<u>Low</u>	<u>Median</u>	<u>High</u>	
Lactic Acid	Eccrine sweat		Negligible		0.05
Ammonia	Eccrine sweat		0.02		
Ammonia	Urea decomposition by bacteria	890	4200	7000	
Phenol	Eccrine sweat	2	10	17	
Iodine	Eccrine sweat toxication		Negligible		
Butyric, Caproic, Valeric Acids	Sebum		Unknown, probably negligible		
Decanoic Acid	Sebum		Negligible		0.03
Lauric Acid	Sebum		Negligible		0.2
Methane	Flatus & breath	49	200	490	
Hydrogen	Flatus & breath	24	100	240	
Hydrogen Sulfide	Flatus	0.007	0.028	0.068	
Unidentified Gases	Flatus	3	11	28	
Carbon Monoxide	Carbon monoxide	18	38	53	

* Numbers refer to amount estimated to reach the atmosphere.

**Based upon attainment of equilibrium vapor pressure.

TABLE 13

TRACE CONTAMINANTS FROM BIOLOGICAL
SOURCES DURING 14-DAY MISSION

<u>Trace Contaminant</u>	<u>Symbol</u>	<u>Amount</u> <u>Micromoles</u>
Ammonia	NH ₃	4,200,000
Methane	CH ₄	206,000
Hydrogen	H ₂	100,800
Carbon Monoxide	CO	53,900
Phenol	PH	10,080

Selecting Trace Materials for Use in Trace
Material Control Unit

A numerical comparison of toxicity ratings for trace materials was required in order that substitutions could be made for the 12 trace materials from the Stabilization and Control System to arrive at a simulation program based on a lesser number of trace materials. There is no established procedure for combining all toxicity data related to a given chemical species to arrive at a relative measure of toxicity. Yet, some scheme had to be devised to obtain an over-all rating for each compound so that trace contaminants could be given a numerical classification. The classification developed for this purpose was based upon the following factors:

TLV Rating	The threshold limiting value set by the American Conference of Governmental Industrial Hygienists.
Toxicity Rating*	0 - No harm. 1 - Slight reversible changes. 2 - Moderate reversible or irreversible changes not causing permanent injury. 3 - Severe effects possibly causing death or permanent injury after short exposure to small quantities.
Site Rating	Rated as 1 if local. Rated as 2 if systemic.
Speed Rating	Rated as 1 if chronic. Rated as 3 if acute.
Route Rating	Rated as 1 if by inhalation or if an irritant. Rated as 5 if by absorption. Rated as 10 if by ingestion.

*As rated by Sax, N. Irving, "Dangerous Properties of Industrial Materials", Reinhold, 2nd Edition (1963).

The ratings for site, speed, and route are original to this program, as is the summation of ratings given below over multiple modes of action:

$$\text{"Relative Toxicity"} = \frac{10,000}{\text{TLV}} \sum \frac{(\text{Toxicity}) (\text{Site}) (\text{Speed})}{\text{Route}}$$

An example of the use of the above equation is given for the case of carbon monoxide which has a TLV of 100, and the following toxicity ratings:

Toxicity Ratings for Carbon Monoxide

Acute				Chronic	
Local			Systemic	Local	Systemic
(a)	(b)	(c)	(d)	(e)	(f)
Irritant	Ingestion	Inhalation	Inhalation	Irritant	Inhalation
0	0	0	3	0	1

Summing for carbon monoxide:

$$\frac{(\text{Toxicity})}{(\text{Rating})} \times \frac{(\text{Site})}{(\text{Rating})} \times \frac{(\text{Speed})}{(\text{Rating})} \div \frac{(\text{Route})}{(\text{Rating})}$$

from above tabulation

$$\begin{aligned}
 (a) \text{ No harm } (0) \times \text{ local } (1) & \times \text{ acute } (3) \div \text{ irritant } (1) = \frac{0 \times 1 \times 3}{1} = 0 \\
 (b) \text{ " " } \times \text{ " } & \times \text{ " } \div \text{ ingestion } (10) = \frac{0 \times 1 \times 3}{10} = 0 \\
 (c) \text{ " " } \times \text{ " } & \times \text{ " } \div \text{ inhalation } (1) = \frac{0 \times 1 \times 3}{1} = 0 \\
 (d) \text{ Severe } (3) \times \text{ systemic } (2) & \times \text{ " } \div \text{ inhalation } (1) = \frac{3 \times 2 \times 3}{1} = 18 \\
 (e) \text{ No harm } (0) \times \text{ local } (1) & \times \text{ chronic } (1) \div \text{ irritant } (1) = \frac{0 \times 1 \times 1}{1} = 0 \\
 (f) \text{ Slight } (1) \times \text{ systemic } (2) & \times \text{ " } \div \text{ inhalation } (1) = \frac{1 \times 2 \times 1}{1} = 2 \\
 & \sum = 20
 \end{aligned}$$

Thus, for carbon monoxide,

$$\text{"Relative Toxicity"} = \frac{10,000}{\text{TLV}} \sum = \frac{10,000}{100} \times 20 = 2,000.$$

Table 14 is a compilation of toxicity criteria for trace materials. The data were used to obtain "relative toxicity" ratings for other materials in the manner illustrated above for carbon monoxide. The normalized ratings are given in Table 15. These ratings were used to make substitutions for some of the trace materials to arrive at a simulation program for the entire inventory based on a lesser number of trace materials. Substitutions were made within chemical families where possible. This was done in deference to the opinion that numerical toxicity ratings are not truly quantitative and should be used with due regard taken of the known chemical and physiological properties of each material.

CHARACTERIZATION

Compound (List includes those appearing once or more as major constituents & 5 or more times as minor constituents)

	Formula	Prevalence Ranking*	Molecular Weight	Temperature 760 mm (°C)	Dipole Moment ($\mu \times 10^{18}$ esu)	TLV (PPM)	Act
Carbon Monoxide	CO	1	28	-192	0.1	100	
Carbon Dioxide	CO ₂	2	44	-78s	0	5000	
Acetone	CH ₃ COCH ₃	3	58.1	56	2.89	1000	
Ethyl Formate	HCOOC ₂ H ₅	3	74.1	58	1.93	100	
Methyl Acetate	CH ₃ CO ₂ CH ₃	3	74.1	54	1.72	200	
n-Butyl Alcohol	CH ₃ (CH ₂) ₃ CH ₂ OH	4	74.1	117	1.67	100	
Methyl Isobutyl Ketone	(CH ₃) ₂ CHCH ₂ COCH ₃	5	100.2	118	(2.8)	100	
m-Xylene	C ₆ H ₄ (CH ₃) ₂	6	106.2	139	(0.3)	200	
o-Xylene	C ₆ H ₄ (CH ₃) ₂	6	106.2	144	0.62	200	
p-Xylene	C ₆ H ₄ (CH ₃) ₂	6	106.2	138	0	200	
Ethyl Alcohol	CH ₃ CH ₂ OH	7	46.1	79	1.70	1000	
iso Propyl Alcohol	CH ₃ CHOHCH ₃	8	60.1	82	1.60	400	
Toluene	C ₆ H ₅ CH ₃	9	92.1	111	0.36	200	
Propionaldehyde	CH ₃ CH ₂ CHO	10	58.1	49(740)	2.72	?	
Benzene	C ₆ H ₆	11	78.1	80	0	25	
Ethylbenzene	C ₆ H ₅ C ₂ H ₅	12	106.2	136	0.59	200	
Trichloroethylene	CHCLCCL ₂	13	131.4	87	(1.5)	100	
Carbon Disulfide	CS ₂	14	76.1	46	0	20	
Acetaldehyde	CH ₃ CHO	15	44	21	2.72	200	
n-Valeraldehyde	C ₄ H ₉ CHO	16	86.1	103	(2.72)	?	
n-Butyraldehyde	CH ₃ (CH ₂) ₃ CHO	17	72.1	76	2.72	?	
Methylethyl Ketone	CH ₃ COCH ₂ CH ₃	18	72.1	80	(3)	200	
tert-Butyl Alcohol	(CH ₃) ₃ COH	19	74.1	83	16	100	
Heptane	CH ₃ (CH ₂) ₅ CH ₃	20	100.2	98	0	500	
iso Butyl Alcohol	(CH ₃) ₂ CHCH ₂ OH	21	74.1	108	1.64	?	
Mesitylene	C ₉ H ₁₂	22	120.2	165	0	?	
Methyl Methacrylate	CH ₂ C(CH ₃)COOCH ₃		100.1	101.0	(1.8)	400	
Freon 114	CClF ₂ CClF ₂		171	3.5	0	1000	
Ethylene Dichloride	CH ₂ CLCH ₂ CL		99.0	83.5	0	50	
Vinylidene Chloride	CH ₂ CCL ₂		97.0	31.6	(2.05)	500	
Methylene Chloride	CH ₂ CL ₂		84.9	40.1	0	500	
Ammonia	NH ₃		17.0	-33.35	1.46	100	
Methane	CH ₄		16.0	-161.5	0		
Hydrogen	H ₂		2.0	-259	0		
Phenol	C ₆ H ₅ OH		94.1	181.9	1.7	5	

* Prevalence Ranking -- those which are rated appeared once or more as major constituents and 5 materials at 200°F in 5 PSIA oxygen. Reference 2.

**Data from Sax, "Dangerous Properties of Industrial Materials", Reinhold, 2nd Edition (1963).

0 - No harm.

1 - Slight-readily reversible.

2 - Moderate-reversible or irreversible. No death or permanent injury.

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LE 14

OF TRACE MATERIALS

Toxicity Criteria**									
Acute (short duration exposure or dose-seconds, minutes, hours)						Chronic (long duration, days, months, years)			
Local			Systemic			Local	Systemic		
Irritant	Ingestion	Inhalation	Ingestion	Inhalation	Skin Absorption	Irritant	Ingestion	Inhalation	Skin Absorption
0	0	0		3		0		1	
0	0	0		1		0		1	
1	2	2	2	2	2	1	1	1	1
2		2		2		Unknown	U	U	U
1			2	2	2	U	2	2	2
1	2		2	2	2	U	1	1	1
2	2	2	3	3		U	U	U	U
1				1		1		1	1
1				1		1		1	1
1				1		1		1	1
1			2	2	1	1	1	1	1
1	1	1	2	2		U	1	1	
	2		2	2	1	1	2	2	2
2	2	2	U	U	U	U	U	U	U
2	1	1	2	2	2	0	3	3	3
2			2	2	2	U	U	U	U
1	1	1	2	3	2	1		1	1
1	1	1	3	3	3	U	3	3	3
3	3	3	2	2		1	2	2	
2	2	1	2	2		1	U	U	U
1	1	1		2		1	U	U	U
1			2	2	2	U	U	U	U
3	3	2	2	2		1	U	U	U
U	U	U	2	3		U	U	3	
1	1	1	1	1		U	1	1	
1		2		1		U	U	U	U
3	3	3	3	3		2	3	3	2
3				2		2	U	U	U
2	2	2	2	3	2	U	1	1	1
3	3	3	U	U	U	1	U	U	U
0		0		1		0		1	
0		0		1		0		0	0
3	3	3	3	3	3	2	2	2	2

or more times as minor constituents among compounds outgassed from certain organic engineering

3 - High -- may cause death or permanent injury with small dose.
 U - Unknown -- no information on humans considered valid.

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TABLE 15

"RELATIVE TOXICITY" RATINGS OF TRACE CONTAMINANTS

<u>Trace Contaminant</u>	<u>Symbol</u>	<u>"Relative Toxicity"*</u>
Carbon Monoxide	CO	100
Acetone	AC	14.4
Ethyl Formate	AC ⁺	120
Methyl Acetate	AC ⁺	60
n-Butyl Alcohol	NBAL	110
Methylene Chloride	MC	37
Methyl-n-Butyl Ketone	MIBK	160
o- m- or p-Xylene	XYL	30
Ethyl Alcohol	EAL	10.5
i-Propyl Alcohol	IPAL	28
Toluene	TOL	62
Benzene	BEN	759
Ethyl Benzene	EBE	62
Trichloroethylene	TCE	143
Carbon Disulfide	CDS	952
Acetaldehyde	ACA	95
Methyl Ethyl Ketone	MEK	48
t-Butyl Alcohol	TBAL	95
Methyl Methacrylate	MMC	9.4
Cumene	CUM	30 (est.)
Freon 114	F114	7.5
Ethylene Dichloride	EDC	480
Vinylidene Chloride	VDC	23 (est.)
Ammonia	NH ₃	36.8
Methylene Chloride	MC	37 (based on vinyl chloride)
Methane	CH ₄	---**
Hydrogen	H ₂	---**
Phenol	PH	2000

* Normalized to a value of 100 for carbon monoxide.

**Not rated -- simple asphoxiants offering fire and explosion hazards.

+ Materials expressed also as acetone.

Generation Rate Patterns

The generation rate pattern for the SCS will be used to illustrate the method of simulating generation rate patterns with the trace material control unit. The amounts of trace materials and their "relative toxicity" ratings are compiled in Table 16 from corresponding data in Tables 8 and 15. Substitute trace materials and their "relative toxicities" are also listed in Table 16, and a final summation is made over the quantities of substitute materials. This procedure limited to five the number of trace materials required to program the control unit for simulation of generation rates from the SCS.

TABLE 16.

FINAL GENERATION RATE PATTERN FOR SCS SYSTEM (14-DAY TOTALS)

Actual Trace Material		Substitute Trace Material		Summation Over	
Symbol*	Amount, Micromoles	Name or Symbol	"Relative Toxicity"	Substitute Trace Materials Material Amount, μ Moles	Material Amount, μ Moles
IPAL	7,510	NBAL	110	1,910	Acetone 38,000
CO	5,465	CO**	100	5,465	CO 5,465
AC	3,109	Acetone	14.4	26,000	NBAL 2,064
MIBK	1,044	Acetone	14.4	11,600	HEP 480
XYL	720	BEN***	759	29	BEN 98
TOL	672	BEN	759	56	UNK (1,180)
HEP	480	HEP**	19	480	
EAL	203	NBAL	110	20	
NBAL	134	NBAL**	110	134	
CUM	105	BEN	759	4	
EBE	102	BEN	759	9	
MEK	90	Acetone	14.4	310	
MMC	40	Acetone	14.4	61	
UNK	1,180	--	--	(1,180)	

* See Table 14 for names corresponding to these symbols.

** Actual trace material used in TMCU.

***Benzene.

It was shown in the section of this report on "Trace Materials Not Generated by SCS" that there will be approximately three times more electronic gear than represented by the SCS contributing to trace material contamination. It is apparent that a complete generation rate pattern will result from multiplying the generation rate profile for the SCS by three and adding the additional trace contaminants from materials and processes (Table 9), and from biological sources (Table 13). This is done in Table 17 to present a final generation rate pattern for the entire mission covering all sources of contamination.

The final step in this analysis requires that the generation rate patterns be translated into useful and practical programs for the operation of the TMCU.

It will be noted that no substitutions have been made for heptane, methane, and hydrogen although they are all much alike in chemical and physiological behavior. It is suggested that they all be used in the TMCU because substitutions for such large amounts of materials might lead to gross errors.

TABLE 17

FINAL GENERATION RATE PATTERN FOR MATERIALS, PROCESSES AND MEN (14-DAY TOTALS)

<u>Actual Trace Material</u>		<u>Substitute Trace Material</u>		<u>Summation Over</u>	
<u>Symbol</u>	<u>Amount,</u>	<u>"Relative Toxicity"</u>	<u>Name or Symbol</u>	<u>Amount</u>	<u>Substitute Trace Materials</u>
	<u>μ Moles</u>				
SCS*					
(See Table 15)					
				Acetone	114,000
				CO**	16,395
				NBAL	6,192
				HEP	1,440
				BEN**	294
				UNK***	3,540

Material and Process Sources Other than Electronic Gear

F114	1,218,000	--	(F114)	1,218,000	F114	1,218,000
EDC	8,120	480	(EDC)	8,120	EDC	8,200
VDC	406	23 (est.)	EDC	33	BEN**	203
MC	406	37	EDC	47		
BEN	203	--	(BEN)	203		

Biological Sources

NH ₃	4,200,000	--	(NH ₃)	4,200,000	NH ₃	4,200,000
CH ₄	206,000	--	(CH ₄)	206,000	CH ₄	206,000
H ₂	100,800	--	(H ₂)	100,800	H ₂	100,800
CO	53,900	--	(CO)	53,900	CO**	37,500
PH	10,080	--	(PH)	10,080	PH	10,080
UNK	1,200	--	--	1,200	UNK***	1,200

* Represents all electronic gear. Quantities are three times the amounts listed in Table 15.

** These materials are generated by more than one source: total CO = 16,395 + 53,900 ≈ 53,900 μ moles
total BEN = 294 + 203 ≈ 500 μ moles.

***The existence of these two groups of unknown contaminants from electronic gear and biological sources suggests the need for further analytical studies to identify these trace materials.

Programming the Trace Material Control Unit

The absolute generation rates presented in Table 16 must be integrated into programs for operation of the Trace Material Control Unit to simulate contamination of a system which does or does not involve a trace material sink. These programs are developed in the following sections of the report. Their development required (1) the use of a simple mathematical model simulating the depletion process, (2) the selection of a reasonable leak rate or circulation rate through the Environmental Control System (ECS), and (3) the definition of complete systems adapted for use with the TMCU.

Simulation of Depletion Processes

The possible depletion factors are gas sampling, condensation, decompression, operation of the Environmental Control System (ECS), and leakage. Gas sampling is analogous to removal of trace contaminants by the ECS or by leakage. If all three are 100 percent effective in the removal of trace materials, gas sampling can be included as an insignificant contribution to the other two depletion factors. Condensation is not expected to be a significant depletion factor providing there is good circulation coupled with an efficient ECS, as appears to be the case. Condensation would be a major depletion factor to a closed system containing no other sinks for trace materials. This does not appear to be a practical situation to simulate. The system could neither be controlled nor used to any purpose. Decompression is a special event which would be handled as a purging followed by a new approach to steady state conditions. Thus, ECS operation and leakage constitute the depletion factors treated for modification of generation rate patterns.

Leakage and ECS operation can be treated alike in that both remove trace contaminants at rates proportional to the concentration of contaminant. Assuming complete mixing in the cabin, the steady state concentration of any contaminant can be obtained, using appropriate units, from:

$$D_{ss} = r C_{ss}$$

[2]

where r = leak rate or rate of circulation through the ECS,

D_{ss} = depletion rate at steady state.

The above condition is preceded by a transient or unsteady-state process leading to the steady-state concentration. This process can be treated as a simple dilution problem having a particular solution corresponding to the steady-state condition described above.

If R = rate of generation of trace material

Q = rate of generation of clean air as by
 (1) leakage and replacement of contaminated air, or
 (2) flow through the ECS, in cfm for example

v = volume of system

t = time

C = concentration,

$$\text{then } \frac{dc}{dt} = \frac{R}{v} - \frac{QC}{v} \text{ or } \frac{vdc}{dt} + QC = R$$

[3]

This homogeneous linear first order differential equation has a particular solution for the steady-state condition when $\frac{dc}{dt} = 0$:

$$R = Q C_{ss}$$

$$\text{It has the general solution, } C = \frac{R}{Q} \left(1 - e^{-\frac{Qt}{v}} \right)$$

[4]

Selection of Reasonable Leak Rate and Circulation
Rate through Environmental Control System

An estimation of circulation rate through the Environmental Control System, ECS, is based upon a rate sufficient to maintain the cabin CO₂ level at one percent, or at a partial pressure of 7.66 mm Hg. The uncontrolled accumulation of CO₂⁽⁵⁾ with time varies with cabin volume because of man's accommodation to CO₂ and retention of CO₂ in his system. In 1000 liters, the pressure of CO₂ from one man reaches 36 mm Hg in three hours. This corresponds to an average generation rate of 200 liter-mm Hg per minute. For a volume of 2000 liters per man as in the case of the Apollo C/M, the generation rate is about 250 liter-mm Hg per man-minute. Under this condition, a circulation rate of 33 liters per minute through the ECS would be sufficient to maintain a steady state partial pressure of CO₂ of 7.6 mm Hg.

The total circulation required for three men would be 99 liters per minute, assuming no other sources of CO₂, and assuming 100 percent efficiency of the ECS. This amounts to 3.5 cfm or 1.65 percent per minute. For purposes of this study, the value of 3.5 cfm is used either as a leak rate or rate of circulation through the ECS.

The time to reach steady state based on either leak rate or circulation rate can be calculated from the equation:

$$C = \frac{R}{Q} \left(1 - e^{-\frac{Qt}{V}} \right)$$

where C = "concentration" of CO_2 in mm Hg

R = rate of generation of $\text{CO}_2 \approx 760$ l-mm Hg/min

Q = rate of generation of clean air ≈ 100 l/min

t = time in minutes

v = volume = 6,000 l

The time to arrive within one percent of the steady state concentration is 4.6 hours.

The units used in the above calculation are less convenient than:

C = μ moles/cu ft

R = μ moles/hour

Q = cu ft/hour = $60 \times \text{cfm} = 60 \times 3.5 = 210$

v = cu ft of system = 212

t = hours

Noting that $Q \approx v$ or $Q/v \approx 1$, the equation takes the simpler form:

$$C = \frac{R}{Q} (1 - e^{-t}) \quad [5]$$

A TMCU Program for Closed System
without Trace Material Sinks

Imagine a closed system with zero dumping rate. The TMCU is to be programmed to simulate the constant rate of increase of trace material concentration in a closed system having no sinks for removal of trace contaminants. In this case, the pulse rate will be constant and equal numerically to the calculated generation rate in μ moles per hour.

Table 18 contains a compilation of generation rates for all trace materials (Column 3). It will be observed that only ammonia calls for a generation rate or pulse rate slightly exceeding the designed capability of the Trace Material Control Unit, 10,000 μ moles per hour or pulses per hour.

In view of the probability that no system will be free from condensation and adsorption, it is unlikely that the final concentration of Column 4 (Table 18) will be attained after 14 days of generation into a closed system. The error might, in fact, be extremely great in the cases of benzene, heptane, n-butyl alcohol, and phenol, which are generated at low rates and never reach high concentrations.

It is suggested, therefore, that the closed system be simulated by an open-loop system from which trace materials are dumped continually at a rate proportional to their concentration, i.e. at a constant-volume rate. The pulse rate from the TMCU will have to exceed the calculated rate of generation of trace materials by the rate of loss by dumping:

Pulse rate = generation rate + rate of loss by dumping.

The rate of loss by dumping will be directly proportional to concentration. The concentration, in turn, must vary from zero at zero time to a final value at 336 hours of:

$$\frac{\text{generation rate (in } \mu \text{ moles/hour) } \times 336 \text{ hours}}{\text{Volume (212 cu ft)}}$$

TABLE 18

CALCULATED CONCENTRATIONS OF TRACE MATERIALS

<u>Material</u>	<u>Total Amount for 14-Day Mission, u Moles</u>	<u>Average Generation Rate, u Moles/Hour</u>	<u>Final Concentration with No Sinks*, u Moles/Cu Ft</u>	<u>Steady State Concentration**</u>	
				<u>u Moles/Cu Ft</u>	<u>ppm</u>
NH ₃	4,200,000	12,500	19,800	59.4	52.5
F114	1,218,000	3,620	5,740	17.3	15.3
CH ₄	206,000	613	970	2.9	2.6
Acetone	114,000	340	538	1.7	1.5
H ₂	100,800	300	475	1.4	1.2
CO	53,900	160	254	0.76	0.76
Phenol	10,080	30	47.5	0.14	0.12
EDC	8,200	24.4	38.7	0.12	0.11
NBAL	6,190	18.4	29.2	0.088	0.08
HEP	1,440	4.3	6.8	0.020	0.018
BEN	497	1.5	2.3	0.0071	0.0063

* For total output of generator into 212 cu ft.

**Same as above, but with either a leak rate of 3.5 cfm or circulation through 100 percent efficient ECS at 3.5 cfm.

Thus, the concentration is directly proportional to time. Accordingly:

$$\text{Pulse rate} = \text{generation rate} + bt = a + bt.$$

Taking Freon 114 as an example, its generation rate is 3620 μ moles per hour. From this, $a = 3620 \mu$ moles per hour. The final concentration at 336 hours will be $(3620 \times 336)/212$ or 5740 μ moles per cu ft, at which time the rate of loss by dumping is:

$$\begin{aligned} Cr &= 5740 \mu \text{ moles/cu ft} \times 3.5 \text{ cfm} \times 60 \text{ min/hr} \\ &= bt \end{aligned}$$

$$\therefore b = 3590, \text{ and}$$

$$\text{Pulse rate} = a + bt = 3620 + 3590 t.$$

Table 17 lists the data necessary to calculate the constants a and b , and Table 19 outlines the program for the trace material control unit for all trace materials in terms of the constants a and b . The program is displayed graphically for BEN, HEP, NBAL, EDC, and PH in Figure 5. For these materials, the final pulse rates do not exceed the designed capabilities of the TMCU. This open-loop system will be useful for studies of these materials without much danger of failure due to adsorption or condensation.

If the simulation is to include all the trace materials at one time, the open-loop system will still be more reliable. To use it, the TMCU must be designed to put out from over four moles per hour of ammonia to only 1.5 μ moles per hour of benzene.

TABLE 19

PROGRAM FOR TMCU TO SIMULATE SYSTEM
HAVING NO TRACE MATERIAL SINKS*

<u>Material</u>	<u>Initial Pulse Rate, a, or Actual Generation Rate in μ Moles/Hr</u>	<u>Final Concentration μ Moles/Cu Ft</u>	<u>$b = \frac{d(PR)**}{dt^2}$ Pulses/Hr²</u>	<u>Final Pulse Rate, Pulses/Hr</u>
NH ₃	12,500	19,800	12,360	4,170,000
F114	3,620	5,740	3,590	1,210,000
CH ₄	613	972	606	205,000
Acetone	340	539	336	113,000
H ₂	300	476	297	100,260
CO	160	254	158	53,500
PH	30	47.6	30	8,490
EDC	24.4	38.7	24.2	8,140
NBAL	18.4	29.2	18.2	6,114
HEP	4.3	6.82	4.2	1,440
BEN	1.5	2.38	1.5	500

* Based on open-loop system having a dumping rate of 3.5 cfm and volume of 212 cu ft.

**Equals (final concentration) (3.5/336).

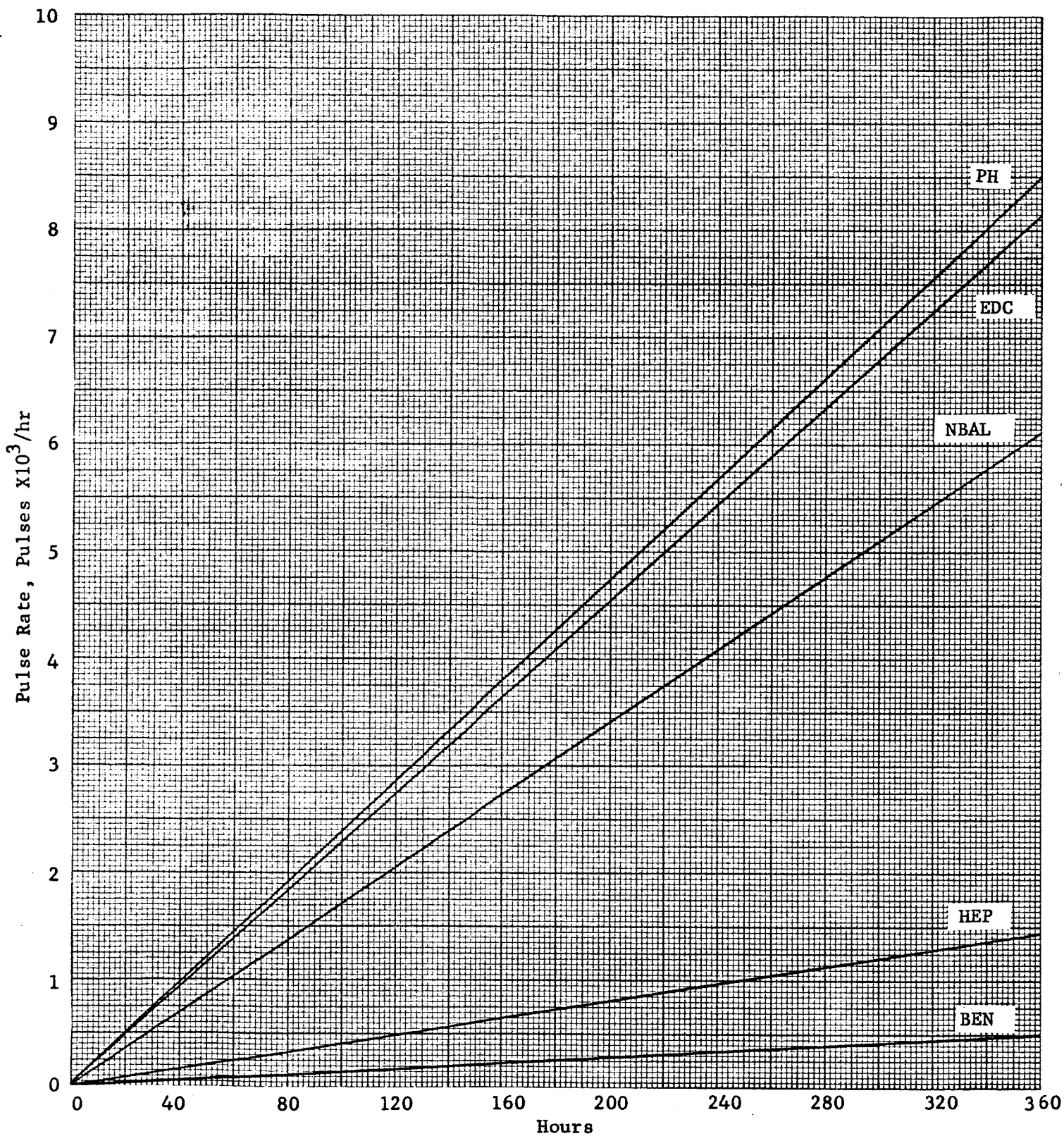


FIGURE 5 PROGRAM OF TMCU TO SIMULATE SYSTEM WITHOUT TRACE MATERIAL SINKS

Programming the TMCU to Simulate a Closed System with Trace Material Sinks

This simulation calls for reliably maintaining steady-state concentrations over a long period of time. This can be accomplished by introducing trace materials into a closed system during the transient period until the steady-state concentration is attained, and then dumping the system while continuing to introduce trace materials at a constant rate equal to the rate of dumping. The transient period for a 212 cu ft system is 4.6 hours when simulating a leak rate of 3.5 cfm or for the same rate of circulation through an efficient environmental control system. The relationship between concentration and time during this transient period was given earlier in the report as:

$$C = \frac{R}{Q} \left(1 - e^{-\frac{Qt}{v}} \right)$$

For purposes of this simulation,

C = concentration of trace contaminant in μ moles/cu ft

R = rate of generation in μ moles/hour

Q = rate of dumping in cu ft/hour = 60 x (3.5 cfm)

t = time in hours.

It follows that,

$$\frac{dm}{dt} = \text{pulse rate} = v \frac{dC}{dt} = R - QC = R e^{-\frac{Qt}{v}}$$

The volume, 212 cu ft, is, by chance, almost equal to Q. Therefore,

$$\text{Pulse rate} = \frac{dm}{dt} = R e^{-t}.$$

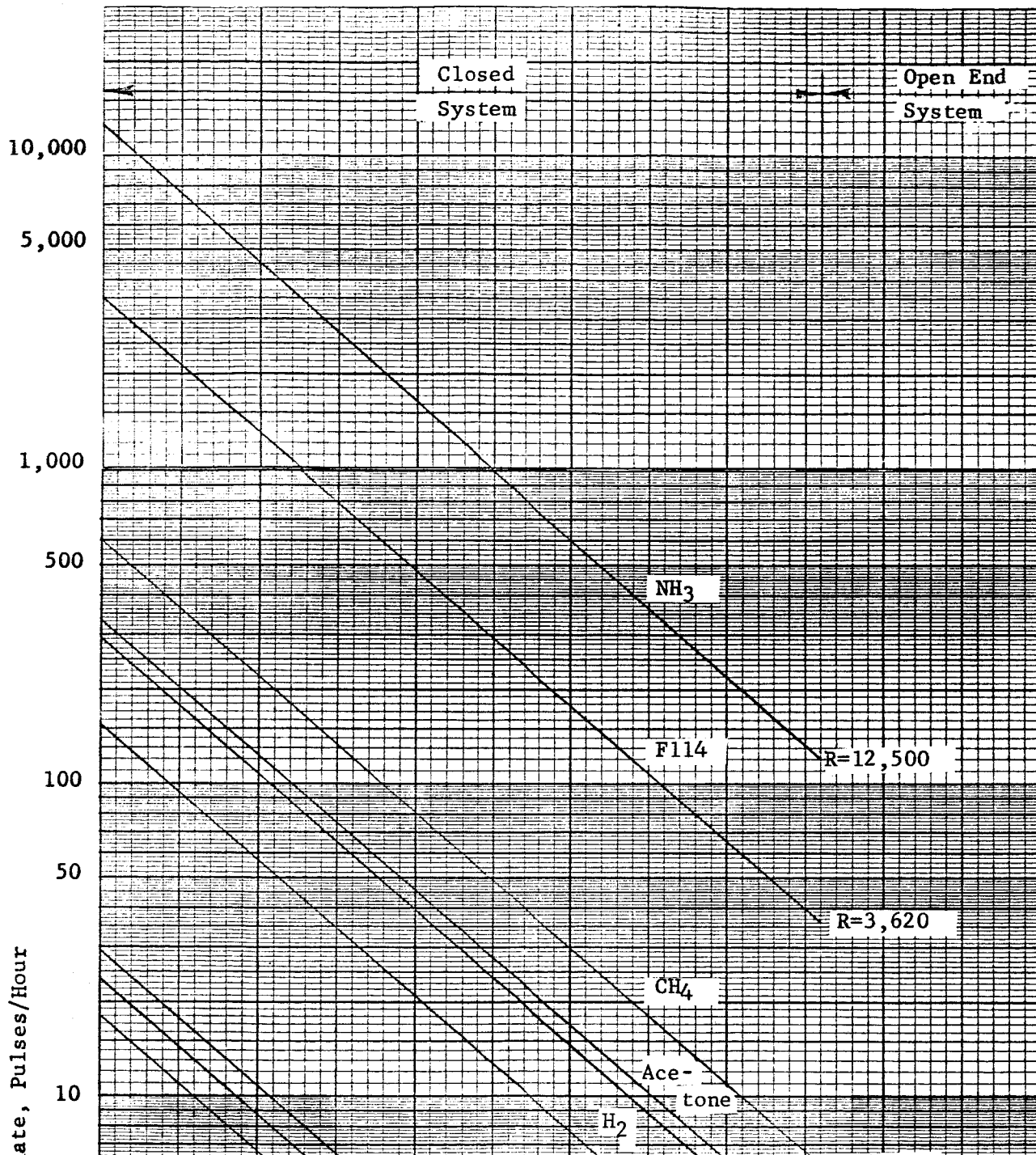
The pulse rate during the first 4.6 hours is a multiple of e^{-t} , the coefficients of e^{-t} being the generation rates of Column 3, Table 18. The pulse rates after 4.6 hours will vary from material to material as:

$$C \text{ (steady state)} = \frac{R}{Q} = \frac{\text{Pulse Rate}}{Q}$$

The steady-state concentrations are given in Table 18. The pulse rate during the transient and steady-state period is presented graphically in Figure 6.

Again, ammonia is the only material to exceed the capabilities of the TMCU (but by only 25 percent). The high generation rate for ammonia may not be realistic. It is a maximum rate obtained by assuming neglect of usual hygiene, and consequent bacterial degradation of the urea content of sweat.

730



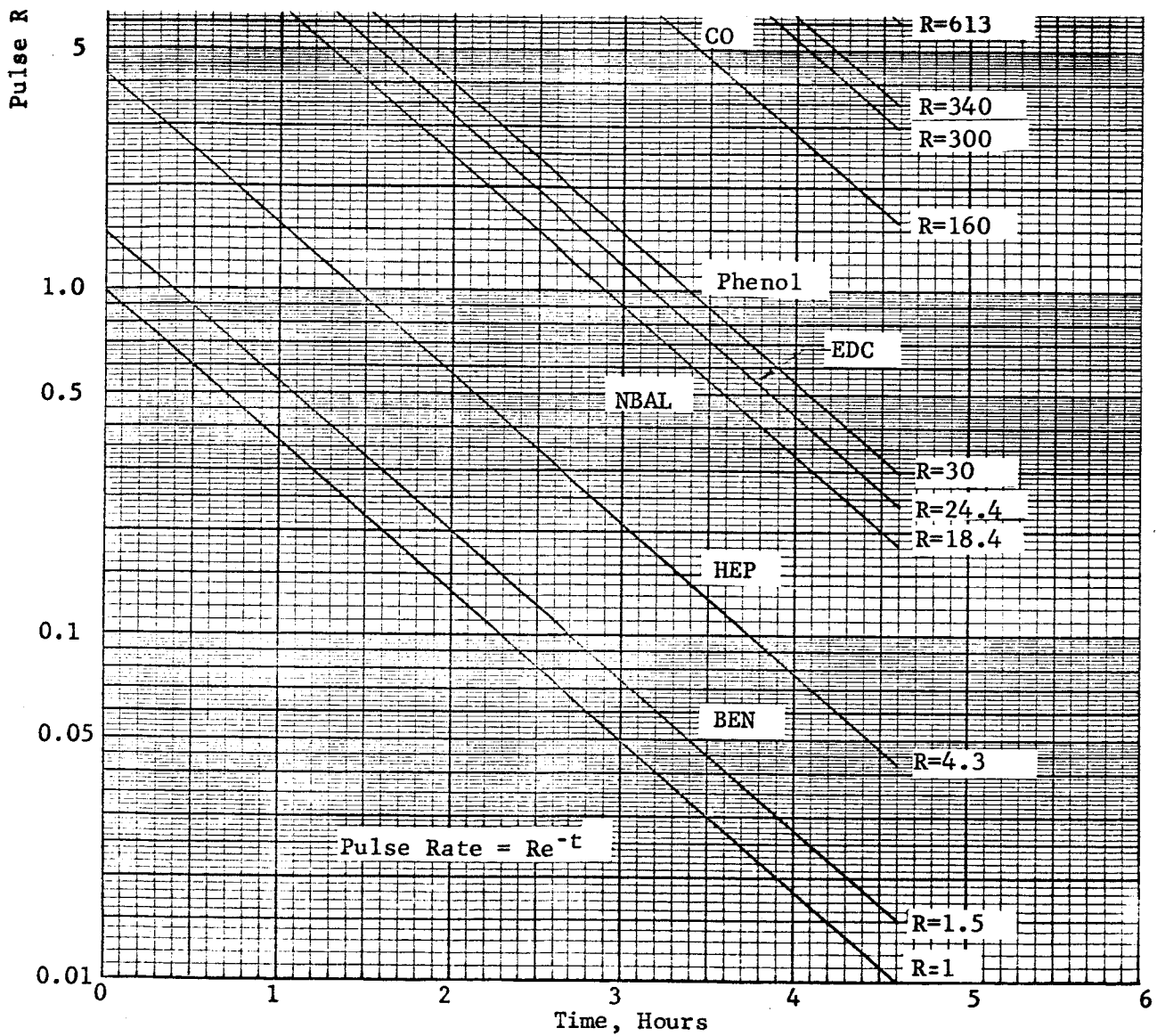


FIGURE 6 PROGRAM FOR TMCU TO SIMULATE LEAK OR OPERATING ECS

REFERENCES

1. Holland, L., Vacuum Deposition of Thin Films, Chapman and Hall Ltd. (1963) page 56.
2. Honeywell, Report on "Gassing and Flammability Testing of Organic Materials for Apollo C/M Stabilization and Control System", A63777A22, dated September 25, 1963, to North American Aviation, Inc.
3. Rothman, S., Physiology and Biochemistry of the Skin, The University of Chicago Press, Chicago (1955).
4. Consolazio, C. F., Nelson, R. A., Matoush, L. O., Harding, R. S., and Canham, J. E., "Nitrogen Excretion in Sweat and its Relation to Nitrogen Balance Requirements," J. Nutrition, 79, pages 399-406 (1963).
5. Webb, P., Bioastronautics Data Book, National Aeronautics and Space Administration, Washington, D. C. (1964).
6. Ostrand, I., "Lactate Content of Sweat", Acta Physiol. Scand., 58, pages 359-367 (1963).
7. Brusilow, S. and Gordes, E. T., "Solute and Water Secretion in Sweat", J. Clin. Invest., 43, pages 477-484 (1964).
8. Altman, P. L. and Dittmer, D. S., Blood and Other Body Fluids, ASDTR 61-199 Aerospace Medical Laboratory, Wright-Patterson Air Force Base, Ohio (1961).
9. Deichmann, W. and Schafer, L. J., "Phenol Studies", Am. J. Clin. Pathol., 12, pages 129-143 (1942).
10. Thurmon, F. M. and Ottenstein, B., "Studies on the Chemistry of Human Perspiration with Especial Reference to its Lactic Acid Content", J. Invest. Dermatol., 18, pages 333-338 (1952).
11. Ottenstein, B., "Contribution to the Chemistry of Sweat", Arch. Dermatol. Syphilis, 191, pages 116-122 (1950).
12. Kligman, A. M. and Shchackli, N., "Pubic Apocrine Glands and Odor", Arch. Dermatol., 89, pages 461-463 (1964).
13. Ikai, K., Sugie, I., and Nitta, H., "Skin Temperature and Amount of Perspiration as Factors Influencing Sebum Excretion," Arch. Dermatol., 88, pages 734-741 (1963).

14. Carruthers, C., Biochemistry of Skin in Health and Disease, Charles Thomas, Springfield, Illinois (1963).
15. Pochi, P. E. and Strauss, J. S., "Sebum Production, Casual Sebum Levels, Titratable Acidity of Sebum and 17-Ketosteroid Excretion in Males with Acne", J. Invest. Dermatol., 43, pages 383-388 (1964).
16. Sunderman, F. W., and Boerner, F., Normal Values in Clinical Medicine, W. B. Saunders Co., Philadelphia and London, page 490 (1949).
17. Haahti, E., "Major Lipid Constituents of the Human Skin Surface", Scand. J. Clin. Lab. Med., Supplement 59, pages 71-108 (1961).
18. Boughton, B., and Wheatly, V. R., "The Fatty Acid Composition of Surface Skin Fat (Sebum) of Normal Human Subjects", J. Invest. Dermatol., 33, pages 49-64 (1959).
19. Porier, P., and Scharpy, A., Traite' d' Anatomie Humaine, 3rd ed., Paris, Masson et Cie, Vol. 2 (1912).
20. Nicolaides, N., and Wells, G. C., "On the Biogenesis of the Free Fatty Acids in Human Skin Surface Fat", J. Invest. Dermatol., 29, pages 423-433 (1957).
21. Murphy, E. L., "Flatus", Conference on Nutrition in Space and Related Waste Problems, National Aeronautics and Space Administration, pages 255-259 (1964).
22. Kirk, E., "The Quantity and Composition of Human Caloric Flatus", Gastroenterology, 12, pages 782-794 (1949).
23. Askevald, F., "Investigations on the Influence of Diet on the Quantity and Composition of Intestinal Gas in Humans", Scand. J. Clin. Lab. Invest., 8, pages 87094 (1956).
24. Beazell, J. M., and Ivy, A. C., "The Quantity of Caloric Flatus Excreted by the Normal Individual", Am. J. Digestive Dis., 8, pages 126-129 (1941).
25. Callaway, D. H., "Discussion: Flatus", Conference on Nutrition in Space and Related Waste Problems, National Aeronautics and Space Administration, pages 261-263 (1964).

26. Murphy, E. L., Personal communication (1965).
27. Sjostrand, T., "Endogenous Formation of Carbon Monoxide", Acta Physiol. Scand., 22, pages 137-141 (1951).
28. Sjostrand, T., "The Formation of Carbon Monoxide by Decomposition of Haemoglobin in Vivo", Acta Physiol. Scand., 26, pages 338-344 (1952).
29. Sjostrand, T., "Endogenous Formation of Carbon Monoxide in Man", Nature, 164, pages 580-581 (1949).
30. Teransshi, R., Buttery, R. G., Lundin, R. E., McFadden, W. F., and Mon, T. R., "Role of Gas Chromatography in Aroma Research", Am. Soc. Brewing Chemists, Proc., pages 52-57 (1963).
31. Gumbmann, M. R., and Burr, H. K., "Volatile Sulfur Compounds in Potatoes", J. Agri. Food Chem., 12, pages 404-408 (1964).
32. Day, E. A., and Anderson, D. F., "Gas Chromatographic and Mass Spectral Identification of Natural Components of the Aroma Fraction of Blue Cheese", loc. cit., 13, pages 2-4 (1965).
33. Rhoades, J. W., and Miller, J. D., "Gas Chromatographic Method for Comparative Analysis of Fruit Flavors", ibid, pages 5-9.